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SENSITIVITY OF GAS CHROMATOGRAPHIC ANALYSIS ON PACKED AND CAPILLARY COLUMNS WITH DIFFERENT TYPES OF DETECTOR UNDER RESOLUTION-NORMALIZED CONDITIONS

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SUMMARY

A comparison of the sensitivity of gas chromatographic analysis on packed and capillary columns coupled with a concentration-sensitive or a mass rate-sensitive detector under resolution-normalized conditions was carried out, the sensitivity being defined as the peak-maximum detector response per unit mass of analyte in the eluted zone. Capillary columns generally yield a substantially higher sensitivity as compared to packed columns under these conditions. With concentration-sensitive detectors the gain in sensitivity produced on replacing a packed column by a capillary one is about two orders of magnitude larger than that produced when a mass rate-sensitive detector is employed.

INTRODUCTION

Modern chromatographic techniques possess both high resolving power and high sensitivity, thus constituting efficient tools for the determination of trace constituents of complex materials. However, in order to take full advantage of the potential offered by these techniques, the conditions for the separation and detection of the components of interest must be optimized. It has long been recognized[1–4] that the separation of a component by chromatography and its dilution in the column are interrelated in such a way that better separations of components are achieved at greater dilutions on passage through the column. Some of the previous studies refer to liquid chromatography[2,3], but the philosophy as well as the relationships derived generally apply to both liquid and gas chromatography.

Whereas in the optimization of the analysis time versus resolution[5] it is sufficient only to consider the column parameters, in sensitivity-resolution optimization the performance characteristics of both the column and the detector have to be taken into account. Different kinds of detector show different behaviours with respect to sensitivity-resolution optimization, the most distinct difference being that between concentration-sensitive and mass rate-sensitive detectors according to Halász's classification[6]. When considering the problems of quantitative analysis by gas chromatography (GC), Guiochon and co-workers[4,7] and others[8,9] discussed the properties of concentration-sensitive and mass rate-sensitive detectors in relation to solute dilution in a column as a function of the column plate number and solute retention.

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Karger *et al.*[3] were the first to formulate unequivocally the complex relationships between the sensitivity of chromatographic analysis, detector properties, column parameters and resolution. We have now followed up that work, the aim to compare the sensitivity of chromatographic analysis under resolution-normalized conditions using packed and capillary columns coupled to a concentration-sensitive or a mass rate-sensitive detector. The lengths of a packed and a capillary column (with the same stationary phase and at the same temperature) were fictively adjusted so as to obtain on both columns the same resolution for a given pair of solutes (e.g., those which are most difficult to separate) at specified (optimized) carrier gas flow-rates, and then the peak-maximum detector responses per unit mass of analyte in the eluted zone, as measured with a concentration-sensitive and a mass rate-sensitive detector, were compared. The comparison proper is carried out by using experimental data of Ettre and March[10].

THEORETICAL

Concept of the sensitivity of chromatographic analysis

Whereas Karger *et al.*[3] and Guiochon and Colin[4] used the detection limit (the minimum mass of analyte for which the peak can be recognized and/or measured in the chromatogram) as a sensitivity criterion, we will employ the peak-maximum detector response per unit mass of analyte in the eluted zone. This quantity characterizes unequivocally the effectiveness with which the chromatographic system (column plus detector) responds to the mass of analyte introduced into the system. Provided the detector response to the analyte is substantially larger than the noise level and the sample is small enough and injected very quickly into the chromatograph, it is not necessary to specify the signal-to-noise ratio and the sample volume with this sensitivity criterion. Hence, more precisely, the peak-maximum detector response, R_i^{max}, per unit mass of analyte in the eluted zone (the mass of analyte i, m_i, introduced into the column), *i.e.*, R_i^{max}/m_i, represents the sensitivity of the chromatographic determination of the mass of analyte.

The sensitivity of detection has been defined by Johnson and Stross[11] as the effectiveness with which a given detector responds to the analyte concentration in the fluid introduced into the detector. Hence, provided the net detector response, R_i, is directly proportional to the solute concentration, c_i, within the range of operation, the quantity R_i^{max}/m_i is given by the product of the sensitivity of detection defined as R_i/c_i and the zone-maximum analyte concentration per unit mass of analyte in the eluted zone:

$$R_i^{max}/m_i = (R_i/c_i)\,(c_i^{max}/m_i) \qquad (1)$$

Actually, the ratio R_i/c_i is the specific detector response to analyte i[8,9]. Provided the eluted zone of the analyte has a gaussian shape, $c_i^{max}/m_i = (1/V_{Ri})\sqrt{N/2\pi}$ where V_{Ri} is the overall retention volume of the analyte as measured at the column temperature, T, and column outlet pressure, P_0, and N is the column plate number[9,12,13]. Thus:

$$R_i^{max}/m_i = (R_i/c_i)\sqrt{N/2\pi}/\,V_{Ri} \qquad (2)$$

Clearly, there is a well defined relationship[9] between the detection limit as specified by Karger *et al.*[3] and Guiochon and Colin[4] and the ratio R_i^{max}/m_i. Designating the detection limit as m_i^{min}, we can write $R_i^{max}/m_i = fG/m_i^{min}$ where G is the baseline noise level (in the same units as R_i) andfis the minimum signal-to-noise ratio required for the analyte peak to be perceptible and/or determinable in the chromatogram (Karger *et al.*[3] used $f = 5$). Hence, we have:

$$m_i^{min} = fG/(R_i^{max}/m_i) \tag{3}$$

If the minimum perceptible and/or determinable analyte concentration in the sample analyzed by chromatography, q_i^{min}, is to be specified, it is possible to use the relation[9]

$$q_i^{min} = fG/[(R_i^{max}/m_i)v_{(i)}^{max}] \tag{4}$$

where $v_{(i)}^{max}$ is the maximum sample volume that can be introduced into the chromatographic column.

Naturally, with splitless sample injection, $v_{(i)}^{max}$ is identical to the overall sample volume injected into the chromatographic apparatus. However, with split injection the volume injected has to be multiplied by the factor $s/(1+s)$ in order to obtain $v_{(i)}^{max}$, s being the ratio of the volumetric carrier gas flow-rates to the column and to the atmosphere as set by the splitter.

Zone-maximum analyte concentration per unit mass of analyte in the eluted zone under resolution-normalized conditions

With a given type of column, the same $H(\bar{u})$ function is supposed to apply for any column length and for any component of the mixture analysed. Further, the effects of the sample volume, the finite rate of sample introduction into the column and the other extra-column zone-broadening effects are assumed to be negligible, and the sensitivity of the detector to be independent of the carrier gas flow-rate.

Consider an n-component mixture to be separated by chromatography, where components 1 and 2, which are most difficult to separate from each other, are to be resolved to a specified number of mean time-standard deviations, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, and where any of the components may be considered as analyte ***i.*** The zone-maximum analyte concentration under these conditions is:

$$\left(\frac{c_i^{max}}{m_i}\right)_{\rho_{12}} = \sqrt{N^*/2\pi}/V_{Ri}^* \tag{5}$$

The asterisks in N^* and V_{Ri}^* indicate that the values of the plate number and retention volume are resolution-normalized, ***i.e.,*** determined by the required resolution, $\rho_{12} = (t_{R2} - t_{R1})/\sigma_{12}$. The quantity N^* can be expressed as

$$N^* = \left(\frac{\rho_{12}}{2}\right)^2 \left(\frac{k_1 + k_2 + 2}{k_2 - k_1}\right)^2 = \left(\frac{\rho_{12}}{2}\right)^2 \left[\frac{k_1 + k_2 + 2}{k_2(1 - \alpha_{12})}\right]^2 \tag{6}$$

where k_1 and k_2 are the capacity ratios of components 1 and 2 on the given column and $\alpha_{12} = k_1/k_2$, and V^*_{Ri} by

$$V^*_{Ri} = (FL^*/\bar{u})\ (1 + k_i) = (\varphi_M L^*/j)\ (1 + k_i) \tag{7}$$

where F is the volumetric carrier gas flow-rate as measured at the column outlet pressure, P_0, and column temperature, T, $\bar{u}$ is the forward velocity of the carrier gas at the mean column pressure, P_0/j, and column temperature, j is the James-Martin compressibility factor, φ_M is the column cross-sectional area occupied by the mobile phase and L^* is a resolution-normalized column length defined by

$$L^* = \bar{H}N^* = \bar{H}\left(\frac{\rho_{12}}{2}\right)^2 \left[\frac{k_1 + k_2 + 2}{k_2(1 - \alpha_{12})}\right]^2 \tag{8}$$

where $\bar{H}$ is the mean plate height of the column. By combining eqns. 5–8 we obtain:

$$\left(\frac{c_i^{max}}{m_i}\right)_{\rho_{12}} = \frac{\sqrt{N^*/2\pi}}{V^*_{Ri}} = \frac{j}{\sqrt{2\pi}} \cdot \frac{1}{\varphi_M \bar{H}\ (1 + k_i)} \cdot \frac{2}{\rho_{12}} \cdot \frac{k_2\ (1 - \alpha_{12})}{k_1 + k_2 + 2} \tag{9}$$

Peak-maximum detector response per unit mass of analyte in the eluted zone under resolution-normalized conditions with concentration sensitive (CSD) and mass rate-sensitive (MRSD) detectors

With concentration-sensitive detectors, the response to analyte i is directly proportional to the analyte concentration in the column effluent. Hence:

$$\left(\frac{R_i^{max}}{m_i}\right)_{\rho_{12},CSD} = a_i\left(\frac{c_i^{max}}{m_i}\right)_{\rho_{12}} = a_i\sqrt{N^*/2\pi}/V^*_{Ri} \tag{10}$$

With mass rate-sensitive detectors, the response to analyte i is proportional to the rate at which the mass of analyte is introduced into the detector, ***i.e.,*** in this case

$$R_i = a_i'\ \mathrm{d}m_i/\mathrm{d}t = a_i' F c_i \tag{11}$$

where R_i is the net detector response to the analyte mass rate $\mathrm{d}m_i/\mathrm{d}t$, a_i' being a proportionality constant. A comparison of eqns. 10 and 11 with eqn. 1 shows that a_i and $a_i'F$ are the specific detector responses R_i/c_i ***(i.e.,*** mass-specific quantities). As $V_{Ri} = Ft_{Ri}$ where t_{Ri} is the retention time of analyte i, it follows for mass rate-sensitive detectors[9]

$$\left(\frac{R_i^{max}}{m_i}\right)_{\rho_{12},MRSD} = a_i' F\left(\frac{c_i^{max}}{m_i}\right)_{\rho_{12}} = \frac{a_i' F\sqrt{N^*/2\pi}}{V^*_{Ri}} = \frac{a_i'\sqrt{N^*/2\pi}}{t^*_{Ri}} \tag{12}$$

where t^*_{Ri} is the resolution-normalized retention time of the analyte. By multiplying eqn. 9 by F, and expressing the latter as $F = \varphi_M \bar{u}/j$, we obtain:

$$F \cdot \frac{\sqrt{N^*/2\pi}}{V^*_{Ri}} = \frac{\sqrt{N^*/2\pi}}{t^*_{Ri}}$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{(\bar{H}/\bar{u})} \frac{1}{(1 + k_i)} \cdot \frac{2}{\rho_{12}} \cdot \frac{k_2(1 - \alpha_{12})}{k_1 + k_2 + 2} \tag{13}$$

Thus, from eqns. 9, 10, 12 and 13 we can write:

$$\left(\frac{R_i^{max}}{m_i}\right)_{\rho_{12},CSD} = a_i \cdot \frac{j}{\sqrt{2\pi}} \cdot \frac{1}{\varphi_M \bar{H}(1 + k_i)} \cdot \frac{2}{\rho_{12}} \cdot \frac{M\,1 - \alpha_{12})}{k_1 + k_2 + 2} \tag{14}$$

$$\left(\frac{R_i^{max}}{m_i}\right)_{\rho_{12},MRSD} = a_i' \cdot \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{(\bar{H}/\bar{u})(1 + k_i)} \cdot \frac{2}{\rho_{12}} \cdot \frac{k_2(1 - \alpha_{12})}{k_1 + k_2 + 2} \tag{15}$$

The fact that the peak-maximum response per unit mass of analyte with mass-rate sensitive detectors is proportional to $1/t_{Ri}$ rather than $1/V_{Ri}$ has very important analytical implications. Eqns. 14 and 15 reveal that, whereas with concentration-sensitive detectors the sensitivity of the chromatographic determination of the mass of analyte is inversely proportional to the product $\varphi_M \bar{H}$, i.e., the void volume of a theoretical plate of the column, with mass rate-sensitive detectors the sensitivity does not depend on φ_M, but is inversely proportional to $\bar{H}/\bar{u}$. This difference manifests itself most markedly when comparing the sensitivities of the chromatographic determination of the mass of analyte on packed and capillary columns coupled with a concentration-sensitive or with a mass rate-sensitive detector.

The quantity $\bar{H}$ is related to the mean-pressure carrier gas velocity, $\bar{u}$, by the Van Deemter equation. Eqn. 14 clearly reveals that with concentration-sensitive detectors the maximum sensitivity of GC analysis is attained at the carrier gas velocity corresponding to the maximum separation efficiency of the column, i.e., at which $\bar{H}$ is minimum. With mass rate-sensitive detectors the situation is not so straightforward; eqn. 15 shows that the value of $\bar{H}/\bar{u}$ must be minimum for the maximum sensitivity of GC analysis. As pointed out by Guiochon et *al.*[7] and Karger *et al.*[3], with mass rate-sensitive detectors the carrier gas velocity required for maximum sensitivity of chromatographic analysis is somewhat higher than that at which $\bar{H}$ is minimum, because the product $N^*\bar{u}$ increases monotonically with increasing ii. It is generally true that with such detectors the optimum velocity in sensitivity-resolution optimization is somewhat higher than that at which $\bar{H}$ is minimum. However, the statement that $N^*\bar{u}$ increases monotonically with increasing $\bar{u}$ applies only to liquid chromatographic columns (incompressible mobile phase). A more detailed analysis of the problem reveals[14] that with GC columns $N^*\bar{u}$ is not monotonic function of ii.

The retention time of component *i* under the above conditions, is

$$t^*_{Ri} = (L^*/\bar{u})\ (1 + k_i) = (N^*\bar{H}/\bar{u})\ (1 + k_i)$$

$$= (\rho_{12}/2)^2\ (\bar{H}/\bar{u}) \left[\frac{k_1 + k_2 + 2}{k_2(1 - \alpha_{12})}\right]^2 (1 + k_i) \tag{16}$$

the time of analysis being given by the retention time of the component eluted last in the chromatogram.

Simplified models

For calculations with experimental data[10] the above models can be simplified as follows:

1. Component *i* is regarded as identical to component 2, and as the component eluted last in the chromatogram.
2. The difference $k_2 - k_1$ is assumed to be negligible compared to k_2 and/or k_1.
3. A resolution $\rho_{12} = 4$ will be required.

Thus, we can write $(1 + k_i)(k_1 + k_2 + 2) \approx 2(1 + k_2)^2$ and $\rho_{12}\sqrt{2\pi} = 4\sqrt{2\pi} \approx 10$, and eqns. 9, 14 and 15 can be rewritten as:

$$\left(\frac{c_2^{max}}{m_2}\right)_{\rho_{12}=4} = \frac{j}{10} \cdot \frac{1 - \alpha_{12}}{\varphi_M \bar{H}} \cdot \frac{k_2}{(1 + k_2)^2} \tag{17}$$

$$\left(\frac{R_2^{max}}{m_2}\right)_{\rho_{12}=4,CSD} = a_i \cdot \frac{j}{10} \cdot \frac{1 - \alpha_{12}}{\varphi_M \bar{H}} \cdot \frac{k_2}{(1 + k_2)^2} \tag{18}$$

$$\left(\frac{R_2^{max}}{m_2}\right)_{\rho_{12}=4,MRSD} = a_i' \cdot \frac{1}{10} \cdot \frac{1 - \alpha_{12}}{\bar{H}/\bar{u}} \cdot \frac{k_2}{(1 + k_2)^2} \tag{19}$$

For the required plate number, column length and the retention time of component 2 (see eqns. 6, 8 and 16) we can now write:

$$(N^*)_{\rho_{12}=4} = \frac{16}{(1 - \alpha_{12})^2}\left(\frac{1 + k_2}{k_2}\right)^2 \tag{20}$$

$$(L^*)_{\rho_{12}=4} = \frac{168}{(1 - \alpha_{12})^2}\left(\frac{1 + k_2}{k_2}\right)^2 \tag{21}$$

$$(t^*_{R2})_{\rho_{12}=4} = \frac{16(\bar{H}/\bar{u})}{(1 - \alpha_{12})^2} \cdot \frac{(1 + k_2)^3}{k_2^2} \tag{22}$$

The term $[1 + k_2)/k_2]^2$ has a maximum value at $k_2 = 1$, whereas $(1 + k_2)^3/k_2^2$ is a minimum at $k = 2$. Hence, as pointed out by Karger *et al.*[3], in sensitivity-resolution optimization the optimum k values are smaller than those in time-resolution optimization. The value of $[(1 + k_2)/k_2]^2$ approaches unity with increasing k_2, being 4 and 2.25 with $k_2 = I$ and $k_2 = 2$, respectively. A comparison of eqn. 21 with the Van Deemter equation reveals that $(L^*)_{\rho_{12}=4}$ is proportional to $1/k_2$ or independent of k_2 if $\bar{H}$ is controlled either by the solute diffusion in the stationary phase or by that in the mobile phase, respectively,

Processing of Ettre's data for packed and capillary columns

The experimental arrangements and conditions employed by Ettre[10] were as follows:

Packed column: 2.4 m × ***2.2*** mm I.D., packed with 10% (w/w) of diethylene glycol succinate (DEGS) on Chromosorb W (So-100 mesh); column temperature 180°C, helium as carrier gas.

Capillary column: 45 m × 0.253 mm I.D., wall-coated open tubular (WCOT) column, DEGS, column temperature 180°C.

Solutes: 1 = methyl oleate; 2 = methyl stearate; $\alpha_{12} = 0.893$,

Other data used in the calculations are summarized in Table I. In addition to the already defined symbols, β is the ratio of the gas-phase and liquid-phase cross-sectional areas in the column, $\bar{u}_{opt}$ is the mean-pressure carrier gas velocity at which $\bar{H}$ is minimum, ***i.e.,*** $\bar{H}_{min}$, $\bar{u}'$ is the mean-pressure carrier gas velocity at which the ratio $\bar{H}/\bar{u}$ begins to approach a constant value according to Fig. 3 in ref. 10 and $\bar{H}'$ is the column plate height corresponding to velocity $\bar{u}'$ (see Fig. 1 in ref. 10). The values of φ_M were calculated from the inner diameters of the columns, the porosity of the column packing being estimated as 0.7. Four variants of calculation are presented, namely, for the packed and capillary columns with lengths adjusted so as to resolve components 1 and 2 to $\rho_{12} = 4\sigma_{12}$ at $\bar{u}_{opt}$ and $\bar{u}'$, each variant being considered with a concentration-sensitive and a mass rate-sensitive detector. The results are summarized in Table II. The values of the column-inlet excess pressure, $\Delta P = P_i - P_0$, were estimated with the aid of the relation $\Delta P = 2P_0(1 - j)/j$, the value ofj being calculated by $j = 1/[\bar{u}L\eta/(2BP_0) + 1]$ where η, B and P_0 are the carrier gas viscosity, specific permeability constant of the column and column outlet pres-

TABLE I

COLUMN PARAMETERS AND CONDITIONS USED IN THE CALCULATIONS

Taken from ref. 10.

Column type	k_1	k_2	β	φ_M *(mm²)*	$\bar{u}_{opt}$ *(cm/sec)*, $\bar{H}_{min}$ *(mm)*	$\bar{H}_{min}/\bar{u}_{opt}$ *(sec)*	$\bar{u}'$ *(cm/sec)*, $\bar{H}$ *(mm)*	$\bar{H}/\bar{u}'$ *(sec)*
Packed	56.8	65.6	10	2.1	6.8 0.71	0.01	20 1.4	0.007
Capillary	5.1	5.7	120	0.05	9.0 0.46	0.005	30 0.7	0.0023

TABLE II

RESULTS OBTAINED BY PROCESSING THE DATA IN TABLE I ACCORDING TO EQNS. 17 22

Column type	$\left(\frac{c_2^{max}}{m_2}\right)_{\rho_{12}=4}$ (cm^{-3})	$\left(\frac{R_2^{max}}{m_2}\right)_{\rho_{12}=4}$ CSD	MRSD	$(N^*)_{\rho_{12}=4}$	$(L^*)_{\rho_{12}=4}$ (mm)	$(t^*_{R2})_{\rho_{12}=4}$ (min)	$(\Delta P)_{\rho_{12}=4}$ (atm)
For $\bar{u}_{opt}$, $\bar{H}_{min}$							
Packed	0.0643	$0.0643a_2$	$0.0158a'_2$	1441	1023	16	0.57
Capillary	58.8	$58.8a_2$	$0.274a'_2$	1931	888	1.08	0.01
Capillary/ packed	913	913	17.34	I.34	0.868	0.0675	0.018
For $\bar{u}'$, $\bar{H}'$							
Packed	0.0158	$0.0158a_2$	$0.0226a'_2$	1441	2017	11.2	3.3
Capillary	37.9	$37.9a_2$	$0.591a'_2$	1931	1352	0.496	0.049
Capillary/ packed	2398	2398	26.14	1.34	0.670	0.0444	0.015
The quantitaties at ii' divided by those at u_{opt}							
Packed	0.246	0.246	1.43	1	1.97	0.70	5.8
Capillary	0.645	0.645	2.16	1	1.52	0.46	4.9

sure, respectively. B values of $3 \cdot 10^{-7}$ cm² and $200 \cdot 10^{-7}$ cm² were assumed[10] for the packed and the capillary columns, respectively.

DISCUSSION

The most remarkable finding is that ensuing from the comparison of the sensitivity of analysis on packed and capillary columns coupled with a concentration-sensitive detector. With the capillary column, the values of $(R_2^{max}/m_2)_{\rho_{12}=4}$ are *ca.* 1000–2000 times those found for the packed column at $\bar{u}_{opt}$ and $\bar{u}'$, respectively. If a mass rate-sensitive detector is used with the capillary column, the values of $(R_2^{max}/m_2)_{\rho_{12}=4}$ are only about 17 or 26 times those found for the packed column. Hence, if a concentration-sensitive detector is employed, the gain in sensitivity obtained on replacing the packed column by the capillary one is about two orders of magnitude larger than that when using a mass rate-sensitive detector. This is mainly due to the approximately 100 times smaller gas-phase cross-sectional area of the capillary column. From eqns. 14 and 15 and/or 18 and 19, it is seen that in systems with a concentration-sensitive detector, $(R_i^{max}/m_i)_{\rho_{12}}$ is inversely proportional to φ_M, whereas with systems involving mass rate-sensitive detectors $(R_i^{max}/m_i)_{\rho_{12}}$ is (theoretically) independent of φ_M. This explains the experimental observation[5–17] that with the combination of a capillary column and a katharometer the minimum detectable and/or determinable mass of analyte is about the same as that observed with systems involving a flame ionization detector (i.e., some tenths of a nanogram), while with a conventional packed column and katharometer the minimum detectable mass of analyte is about two orders of magnitude larger. Hence, one must be very careful when comparing different detection principles in view of the sensitivity of chromatographic analysis.

The lengths of both types of column, necessary to provide the required reso-

lution, are mutually commensurate. However, with the capillary column the analysis time is about an order of magnitude shorter and the pressure drop across the column is almost two orders of magnitude smaller compared to those with the packed column. With both types of column, raising the carrier gas velocity from $\bar{u}_{opt}$ to $\bar{u}'$ leads to a decrease in $(R_2^{max}/m_2)_{\rho_{12}=4}$ if a concentration-sensitive detector is employed and to an increase in $(R_2^{max}/m_2)_{\rho_{12}=4}$ with a mass rate-sensitive detector.

Finally, let us summarize the simplifying assumptions under which the results have been calculated:

(1) $\bar{H}_{opt}$, $\bar{H}'$, $\bar{u}_{opt}$, and $\bar{u}'$ have been assumed to be the same for different lengths of a given column, all the other conditions being kept constant.

(2) a_i and a_i' have been assumed to be independent of the volumetric carrier gas flow-rate.

(3) The extra-column zone-broadening effects have been assumed to be negligible.

Clearly, assumption 1 cannot be true in GC[5]. This approximation is very crude especially in the case of the capillary column, as $\bar{H}_{opt}$, $\bar{H}'$, $\bar{u}_{opt}$, and $\bar{u}'$ data determined for a 45-m column have been applied to a length of about 1 m. As for assumption 2, both a_i and a_i' can be kept virtually constant at different carrier gas flow-rates by use of a stream of make-up gas introduced to the detector. Assumption 3 is very difficult to fulfil with a l-m capillary column. In practice, a longer column would have to be used in order to attain the required resolution. Hence, the data presented in Table II must be taken with certain reservations. However, the approximations that had to be used are not so crude as radically to change the situation. Although the conclusions derived from the calculated results (Table II) have a fairly general validity, it should be recalled that the results themselves apply only to the given set of experimental conditions, *viz.*, the GC separation and determination of methyl oleate and methyl stearate on DEGS columns at 180°C with helium as carrier gas.

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