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Optimum Performance of Capillary GC Columns as a Function of Tube Diameter and Film Thickness under Various Operating Conditions**

Computer Program for Calculation of H-ū Curves and Minimum Analysis Times

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Summary

The *Golay-Giddings* and *Poiseuille* equations are used to derive equations for the calculation of the maximum plate number and minimum time conditions for given columns at fixed, but selectable, outlet pressures. In addition, expressions are presented for the determination of minimum analysis times for separation problems requiring given plate numbers. In this instance, the optimum column length can be calculated as a function of outlet pressure. A Basic computer program, incorporating the equations for the various optima, together with the H-ū curves, is described. Input variables are either column length or desired plate number, column diameter, film thickness, capacity ratio of the solute, column outlet pressure, separation temperature, and carrier gas. The carrier gas viscosity is automatically calculated in the case of hydrogen, helium, or nitrogen. For these gases, and if the solute is a *n*-alkane, the diffusivity of the solute in the mobile phase is calculated. In this case, the carbon number of the solute is needed in the computation.

For high molecular weight polydimethylsilicone phases (*e.g.* SE-30), the program can approximate the diffusivity of *n*-alkanes in the stationary phase at the given temperature as a function of the carbon number. Of course, manually entered values of viscosity and diffusion coefficients can be included in the calculations.

1 Introduction

As a result of advances in column technology, the chromatographer nowadays has a wide-ranging choice of open tubular columns. The column diameters are between "narrow-bore" and "wide-bore" (typically 10 μm and 530 μm), and the stationary phase film thickness can be anywhere between 0 and 10 μm. These columns can be operated over a wide temperature range at outlet pressures from vacuum up to tens of bars.

In order to compare the actual performance of a column with that which can be theoretically achieved, the "coating efficiency" is often used. In this comparison, the pressure drop correction factors (f_1, f_2, see below) and the influence of the liquid phase are neglected. Therefore, the "coating efficiency" is meaningless for narrow-bore and/or thick-film columns [1]. Moreover, in many publications dealing with the speed of analysis obtainable by various columns, the plate numbers are often not constant. Therefore, exact equations for various optimum chromatographic conditions were derived, taking all pressure factors and the liquid mass-transfer term into account.

A computer program was developed for the calculation of these optimum conditions. This program can also calculate plate-height curves, again without neglecting any factors. This contrasts with the computer-constructed plate-height curves as published by *Ingraham et al* [2].

The *Golay-Giddings* plate-height equation for open tubular columns reads [3]:

$$H = \left[\frac{B_o}{u_o} + C_{m,o} u_o \right] f_1 + C_s u_o f_2 \tag{1}$$

In this equation the following symbols are used:

$$B_o = 2 D_{m,o} \tag{2}$$

$$C_{m,o} = \frac{11k^2 + 6k + 1}{24(k+1)^2} \cdot \frac{r^2}{D_{m,o}} \tag{3}$$

$$C_s = \frac{2k}{3(k+1)^2} \cdot \frac{d_f^2}{D_s} \tag{4}$$

$D_{m,o}$ is the binary gas diffusion coefficient of a component in the mobile gas phase at column outlet pressure.

D_s is the diffusion coefficient of the component in the stationary liquid phase.

k is the capacity ratio of the component.

r is the inner column radius.

d_f is the film thickness of the stationary liquid phase.

u_o is the linear gas velocity at the column outlet.

** Dedicated to *Professor Kurt Grob* in recognition of his invaluable contributions to capillary gas chromatography, particularly his work on column quality testing.

Defining $P = p_i/p_o$ as the ratio of column inlet over outlet pressure:

$$f_1 = \frac{9}{8} \frac{(P^4-1)(P^2-1)}{(P^3-1)^2} \tag{5}$$

$$f_2 = \frac{3}{2} \frac{(P^2-1)}{(P^3-1)} \tag{6}$$

If $P \to 1$, both f_1 and f_2 approach the value of 1. If P approaches infinity, $f_1 \to 9/8$ and $f_2 \to 3/(2P)$.

If a pressure gradient exists, decompression of the gas along the column causes its velocity to increase from inlet to outlet. For an ideal gas, both its linear velocity, u, and the binary solute/carrier gas phase diffusion coefficient D_m vary inversely with pressure:

$$u\,p = u_i p_i = u_x p_x = u_o p_o \tag{7}$$

$$D_m p = D_{m,i} p_i = D_{m,x} p_x = D_{m,o} p_o \tag{8}$$

with subscripts i and o denoting inlet and outlet, and x any position in the column.

Introducing the (time-)average linear gas velocity $\bar{u} = f_2 u_o$, the (length-)average pressure $\bar{p} = p_o/f_2$, the atmospheric pressure p_a (e.g. $p_a = 100$ kPa $= 1$ bar), and u_a as the linear gas velocity at unit pressure p_a, eq. (7) can be extended to:

$$\varepsilon = u_i p_i = u_o p_o = \bar{u}\ \bar{p} = u_a p_a \tag{9}$$

Under constant operational conditions ε is a constant. Combination of eqs. (8) and (9) shows:

$$\frac{D_{m,o}}{u_o} = \frac{D_{m,a}}{u_a} = \frac{D_{m,a} p_a}{\varepsilon} \tag{10}$$

with $D_{m,a}$ denoting the binary gas diffusion coefficient at unit pressure p_a. Giving B and C_m the same subscript as the corresponding D_m, eq. (1) can now be rewritten as:

$$H = \left[\frac{B_a p_a f_1}{\varepsilon^2} + \frac{C_{m,a} f_1}{p_a} + \frac{C_s}{\bar{p}} \right] \varepsilon \tag{11}$$

or:

$$\varepsilon = p_a \left[\frac{\dfrac{H\varepsilon}{p_a} - B_a f_1}{C_{m,a} f_1 + C_s \cdot \dfrac{p_a}{\bar{p}}} \right]^{\frac{1}{2}} \tag{12}$$

Note that the square root term represents u_a, the velocity at atmospheric pressure.

Eq. (11) shows that $H = f(\bar{u})$ cannot be straightforwardly evaluated, because ε, $\bar{p}$, and f_1 cannot be expressed generally as simple functions of $\bar{u}$. However, eq. (11) can be rearranged to:

$$\frac{H}{\bar{u}} = \left[\frac{B_a p_a}{\varepsilon^2} + \frac{C_{m,a}}{p_a} \right] f_1 \bar{p} + C_s \tag{13}$$

which can be considered to be exclusively pressure dependent, because ε is given by the Hagen-Poiseuille equation for viscous flow of ideal gases through open tubular columns:

$$\varepsilon = \frac{r^2 p_o^2}{16\eta L}(P^2-1) = \frac{r^2}{16\eta L}(p_i^2 - p_o^2) \tag{14}$$

where η is the dynamic viscosity of the carrier gas, and L is the column length.

For a given column operated at constant outlet pressure p_o, and otherwise constant conditions, the values of f_1, $\bar{p} = p_o/f_2$ and ε are determined by p_i only, see eqs. (5), (6), and (14). Therefore, $H/\bar{u} = f(p_i)$ can be evaluated. Subsequently, for any value of p_i, $\bar{u} = \varepsilon/\bar{p}$ can be calculated from eq. (14). Hence $H = f(\bar{u})$ can be obtained by multiplying eq. (13) by $\bar{u}$.

Eq. (14) can be rearranged to:

$$p_i^2 = \frac{16\eta L}{r^2} \varepsilon + p_o^2 \tag{15}$$

By combination of eq. (11) or (12) with (14) or (15) various optimum conditions can be calculated.

2 Optimum Chromatographic Conditions

Cramers et al. [3] derived the minimum of the H vs. u_o function (at constant p_o) by differentiation of eq. (1) with respect to u_o. The derivatives $\delta f_1/\delta u_o$ and $\delta f_2/\delta u_o$ were calculated as $(\delta f/\delta P)(\delta P/\delta u_o)$. [The latter derivative follows from eq. (14): $\delta u_o/\delta P = u_o 2P/(P^2-1)$.] These authors found an "optimum" outlet velocity, corresponding to minimum plate height, of:

$$u_{o,\text{"opt"}} = \left[\frac{B_o(f_1-y_1)}{C_{m,o}(f_1+y_1) + C_s(f_2+y_2)} \right]^{\frac{1}{2}} \tag{16}$$

After elaboration, their y-factors appear to equal:

$$y_1 = u_o \delta f_1/\delta u_o = f_1 - f_2 P(f_1 - f_2 P) \tag{17}$$

$$y_2 = u_o \delta f_2/\delta u_o = f_2(1 - f_2 P) \tag{18}$$

Note that $f_2 P = p_i/\bar{p}$ and $1 < f_2 P < 3/2$ for $0 < P < \infty$.

Using eqs. (9), (10), (17), and (18), eq. (16) can be rearranged into:

$$\varepsilon_{\min H} = p_a \left[\frac{B_a f_2 P(2f_1 - f_2 P)}{C_{m,a}\ [2f_1 - f_2 P(2f_1 - f_2 P)] + C_s \dfrac{p_a}{\bar{p}}(2-f_2 P)} \right]^{\frac{1}{2}} \tag{19}$$

The same authors showed that $y_1 \ll f_1$ for all practical purposes, meaning that $f_1 \approx f_2 P(2f_1 - f_2 P)$, see eq. (17). ($y_1$ reaches a maximum of 3.19% of f_1 at $P = 2.56$.) Eq. (19) can, therefore, be simplified to:

$$\varepsilon_{\min H} \approx p_a \left[\frac{B_a f_1}{C_{m,a} f_1 + C_s \dfrac{p_a}{\bar{p}}(2-f_2 P)} \right]^{\frac{1}{2}} \tag{20}$$

Often, chromatographers are more interested in minimum time operation. Since the retention time $t_R = (1+k)\,L/\bar{u}$, and $L = NH$, where N represents the column plate number, the ratio $H/\bar{u} = t_R/N/(1+k)$ should be minimized. Hence, eq. (13) should be differentiated. For a given column ($L =$ constant), $\delta(H/\bar{u})/\delta\bar{u} = 0$ yields for $p_o =$ constant.

$$\varepsilon_{L,\min\, t} = p_a \left[\frac{B_a}{C_{m,a}} \cdot \frac{2f_1 + f_2 P(f_1 - f_2 P)}{f_2 P(f_2 P - f_1)} \right]^{\frac{1}{2}} \quad (21)$$

In deriving this result $\delta P/\delta\bar{u}$ and $\delta\bar{p}/\delta\bar{u}$ were calculated as the reciprocals of the respective derivatives of eq. (14), using $\delta\bar{p}/\delta P = \bar{p}(f_2 P - 1).2P/(P^2 - 1)$.

For a given column (L and r constant) and a given carrier gas/stationary phase/solute system at a given temperature (η, $D_{m,a}$, k, D_s, d_f constant) and outlet pressure ($p_o =$ constant), the optimum inlet pressures can now be calculated numerically by interation from eq. (15), using the optimum ε values given by eq. (19), (20), or (21).

Using $\bar{p} = p_o/f_2$ and $\bar{u} = \varepsilon/\bar{p}$, the corresponding H values can then be calculated from eq. (11).

In addition to maximum plate number and separation speed for a given column, there is a third optimum: the minimum analysis time for a given separation problem requiring N plates. For this purpose eq. (15) can be rewritten as:

$$p_i^2 = \frac{16\eta N}{r^2}\, H\varepsilon + p_o^2 \quad (22)$$

and hence the optimum value of $H\varepsilon$ has to be determined. Combination of eqs. (11) and (12) yields:

$$\frac{H}{\bar{u}} = \frac{C_{m,a}\bar{p}\, f_1/p_a + C_s}{1 - B_a p_a f_1/(H\varepsilon)} = \frac{\text{numerator}}{\text{denominator}} \quad (23)$$

Substitution of $H\varepsilon$ from eq. (22) yields another pressure-dependent plate height equation. Therefore, minimum time conditions for $N =$ constant are best calculated (for $p_o =$ constant) via:

$$\frac{\delta(H/\bar{p})}{\delta P} = \frac{\delta(\text{numerator})/\delta P}{\text{denominator}} - \frac{\text{numerator}}{\text{denominator}^2} \cdot$$
$$\cdot \frac{\delta(\text{denominator})}{\delta P} \quad (24)$$

Hence, putting the result equal to zero:

$$\frac{H}{\bar{u}} = \frac{\delta(\text{numerator})/\delta P}{\delta(\text{denominator})/\delta P} \quad (25)$$

Eq. (25) can be evaluated as:

$$\frac{H}{\bar{u}} = \frac{C_{m,a}\dfrac{p_o}{p_a} \left[\dfrac{(f_2 P)^2 + f_1(2 - 2f_2 P)}{f_2(2 - f_2 P)} \right] + C_s}{1 - \dfrac{B_a p_a}{H\varepsilon}\left[\dfrac{(f_2 P)^2 + f_1(2 - 3f_2 P)}{(2 - f_2 P)} \right]} \quad (26)$$

Combination of eqs. (23) and (26) yields:

$$H\varepsilon = -B_a p_a \frac{f_1^2 C_{m,a} + C_s\,(2f_1 - f_2 P)\, p_a/\bar{p}}{C_{m,a}\,(f_1 - f_2 P)} \quad (27)$$

Using eq. (22), p_i can now be numerically calculated by iteration. Once $p_{i,opt}$ is determined, all pressure factors can be calculated and ε is found by substitution of eq. (27) into eq. (12):

$$\varepsilon_{N,\min\, t} = p_a \left[\frac{B_a}{C_{m,a}} \cdot \frac{(2f_1 - f_2 P)}{(f_2 P - f_1)} \right]^{\frac{1}{2}} \quad (28)$$

3 Vacuum Outlet

The equations derived thus far are generally valid for open tubular columns. At $p_o \to 0$, or $P \to \infty$ in general, most equations are greatly simplified. Under $P \to \infty$ conditions, $f_1 \to 9/8$, $f_2 P \to 3/2$, $\bar{p} \to 2p_i/3$, and eq. (14) reduces to:

$$\varepsilon \to \frac{r^2}{16\eta L}\, p_i^2 = \frac{64\eta L}{9r^2}\,\bar{u}^2 \quad (29)$$

Using these limiting values, eq. (11) can be written as:

$$H_{P\to\infty} = \left[\frac{B_a p_a X}{p_i^2} + \frac{C_{m,a}}{p_a X}\, p_i^2 \right]\frac{9}{8} + \frac{3}{2}\,C_s p_i X \quad (30)$$

with $X = 16\eta L/r^2$. Eq. (30) was already derived by *Myers* and *Giddings* [4].

As an alternative,

$$H_{P\to\infty} = \left[\frac{9B_a p_a}{4X\bar{u}^2} + \frac{4C_{m,a}X}{9p_a}\,\bar{u}^2 \right]\frac{9}{8} + C_s\bar{u} \quad (31)$$

Both the exclusively pressure or velocity dependent eqs. (30) and (31) are of practical importance for high pressure or vacuum outlet chromatography. (Computer) fitting of these expressions to experimental data is preferred over fitting of eq. (1), because u_o and B_o are extremely large at vacuum outlet, while $C_{m,o}$ and f_2 are extremely small. Moreover, p_i and $\bar{u}$ can always be measured conveniently.

3.1 Optimum Conditions for Vacuum Outlet

The four eqs. (19), (20), (21), and (28), giving the ε expressions for the various optima, reduce to a set of three

expressions, eqs. (19) and (20) leading to identical results for $P \to \infty$:

$$\varepsilon_{P \to \infty, \, min \, H} = p_a \left[\frac{3B_a}{3C_{m,a} + C_s \frac{p_a}{p_i}} \right]^{\frac{1}{2}} \tag{32}$$

$$\varepsilon_{P \to \infty, \, L, \, min \, t} = p_a \left[\frac{3B_a}{C_{m,a}} \right]^{\frac{1}{2}} \tag{33}$$

$$\varepsilon_{P \to \infty, \, N, \, min \, t} = p_a \left[\frac{2B_a}{C_{m,a}} \right]^{\frac{1}{2}} \tag{34}$$

Eq. (27) reduces to:

$$H\varepsilon = 3 \, B_a p_a \left[\frac{9}{8} + \frac{C_s}{C_{m,a}} \frac{p_a}{p_i} \right] \tag{35}$$

A similar result was already presented in 1962 by *Giddings* [5], who introduced the concept of "critical inlet pressure" p_c:

$$p_c^2 = 18\eta N B_a p_a / r^2 = \frac{9}{8} B_a p_a \, X/H \tag{36}$$

The relation between $H\varepsilon$ and p_c is given by:

$$H\varepsilon = \frac{9}{8} B_a p_a \left[\frac{p_i}{p_c} \right]^2 \tag{37}$$

Using eq. (29), eqs. (32)–(34) can be rewritten as functions of p_i^2. Neglecting the C_s-term in eq. (32) the results are condensed as:

$$p_i^2 = p_a X \left[\frac{n \cdot B_a}{C_{m,a}} \right]^{\frac{1}{2}} \tag{38}$$

with $n = 1$ for minimum plate height conditions, $n = 3$ for minimum time conditions for a given column (L = constant) and $n = 2$ for minimum analysis time for a requested plate number (N = constant). Substitution of eqs. (32)–(34) in eq. (11) yields:

$$\left[\frac{H}{u} \right]_{min \, H} = \frac{3}{2} \frac{p_i}{p_a} C_{m,a} + \frac{3}{2} C_s \tag{39}$$

$$\left[\frac{H}{u} \right]_{L, \, min \, t} = \frac{p_i}{p_a} C_{m,a} + C_s \tag{40}$$

$$\left[\frac{H}{u} \right]_{N, \, min \, t} = \frac{9}{8} \frac{p_i}{p_a} C_{m,a} + C_s \tag{41}$$

The inlet pressures can be expressed as a function of p_c. Eq. (37) can be converted into:

$$p_i^2 = \frac{8}{9} p_c^2 \frac{H}{\varepsilon} \frac{\varepsilon^2}{B_a p_a} \tag{42}$$

which after substitution of eq. (11) yields:

$$p_i^2 = p_c^2 \left[1 + \left[\frac{C_{m,a}}{p_a} + \frac{4}{3} \frac{C_s}{p_i} \right] \frac{\varepsilon^2}{B_a p_a} \right] \tag{43}$$

Insertion of the three ε values from eqs. (32)–(34) gives:

$$p_{i, \, min \, H}^2 = 2 p_c^2 \left[\frac{\frac{p_i}{p_a} C_{m,a} + C_s}{\frac{p_i}{p_a} C_{m,a} + \frac{2}{3} C_s} \right] \tag{44}$$

$$p_{i, L, min \, t}^2 = 4 p_c^2 \left[\frac{\frac{p_i}{p_a} C_{m,a} + C_s}{\frac{p_i}{p_a} C_{m,a}} \right] \tag{45}$$

$$p_{i, N, min \, t}^2 = 3 p_c^2 \left[\frac{\frac{p_i}{p_a} C_{m,a} + \frac{8}{9} C_s}{\frac{p_i}{p_a} C_{m,a}} \right] \tag{46}$$

For thin film columns ($C_s \ll C_{m,a}$), eqs. (44)–(46) reduce to $p_i^2 = n.p_c^2$ with $n = 2$ (minimum H), $n = 4$ (minimum t, L constant) and $n = 3$ (minimum t, N constant). Note that p_c or L are generally not equal in these instances.

The retention time is given by:

$$t_R = N (1+k) \frac{H}{u} \tag{47}$$

Hence, combination with eqs. (39)–(41) yields for vacuum outlet operation of thin-film columns:

$$t_{R, min \, H} = N (1+k) \frac{3}{2} \sqrt{2} \frac{p_c}{p_a} C_{m,a} \tag{48}$$

$$t_{R, L, min \, t} = N (1+k) \, 2 \frac{p_c}{p_a} C_{m,a} \tag{49}$$

$$t_{R, N, min \, t} = N (1+k) \frac{9}{8} \sqrt{3} \frac{p_c}{p_a} C_{m,a} \tag{50}$$

The factors $3 \sqrt{2}/2 : 2 : 9 \sqrt{3}/8$ are $2.12 : 2 : 1.95$.
Substitution of eqs. (36), (2), and (3) in eqs. (48)–(50) gives:

$$t_R = n \, r \, N^{3/2} \frac{11k^2 + 6k + 1}{4(k+1)} \left[\frac{\eta}{p_a D_{m,a}} \right]^{\frac{1}{2}} \tag{51}$$

where n represents the above-mentioned factors from eqs. (48)-(50). Combination of eq. (51) with the well-known resolution equation [6]:

$$R = \frac{1}{4} \frac{k}{k+1} \frac{\alpha-1}{\alpha} N^{\frac{1}{2}} \tag{52}$$

by elimination of N yields:

$$t_R = 16nR^3r \frac{(k+1)^2 (11k^2+6k+1)}{k^3} \times \frac{\alpha^3}{(\alpha-1)^3} \times$$

$$\left[\frac{\eta}{P_a D_{m,a}} \right]^{\frac{1}{2}} \tag{53}$$

where α is the relative retention of two peaks separated with resolution R. Eq. (53) has been published before by Guiochon [7] and Leclercq et al. [8]. The constant 16n equals 24 $\sqrt{2}$ (= 33.9), 32, and 18 $\sqrt{3}$ (3 = 31.2) for the three optima, respectively. Minimum retention times are obtained for k = 1.76 [7].

4 Computer Program

A Basic program was designed to calculate H-u curves and the various optimum chromatographic conditions. The input required is:

– L given (in meter) or N required; the program automatically selects the appropriate mode. If Y = input > 1000 then Y = plate number. This is very convenient, because eqs. (15) and (22) can be interchanged throughout the program.

– r, d_f, the separation temperature T (in Kelvin) and k are requested. (It is advised to employ temperatures at which k is between 1 and 2, i.e. around the optimum value of 1.76.) The carrier gas is asked for. For hydrogen, helium, or nitrogen, the program calculates the viscosity according to Ettre [9]. (His equations 27, 21, and 23, respectively.)

For other gases, or upon the user's request, the program asks for a value of η at a temperature T_1. IF $T_1 \neq T$, η is calculated as:

$$\eta = \eta_{T_1} (T/T_1)^{0.7} \tag{54}$$

– If the carrier gas is H_2, He, or N_2, the program will ask for the carbon number of the solute, provided it is a n-alkane. A subroutine then calculates the binary gas phase diffusion coefficient according to Fuller et al. [10]:

$$D_{m,a} = \frac{T^{1.75} \left[\frac{1}{M} + \frac{1}{14C+2} \right]^{\frac{1}{2}}}{10 \left[V^{1/3} + [16.5C + 1.98(2C+2)]^{1/3} \right]^2} \tag{55}$$

where M and V are the molecular weight and diffusion volume of the carrier gas, and C = carbon number of the n-alkane. (The dimension of $D_{m,a}$ is mm^2/s.)

For other carrier gas/solute combinations, or if the user is not satisfied with the result, $D_{m,a}$ at T_2 is inputted. If $T_2 \neq T$, the program calculates:

$$D_{m,a} = D_{m,a,T_2} (T/T_2)^{1.75} \tag{56}$$

– D_s, T_3 is requested. The program can extrapolate D_s values if $T_3 \neq T$, but the result is only meaningful for n-alkanes on SE-30 phases and within a temperature range of T_3 ± 50 K.

If $T_3 \neq T$ the program will calculate D_s as [11,12]:

$$D_s = D_{s,T_3} \cdot e^{(225-250C)(1/T-1/T_3)} \tag{57}$$

– Finally, p_o is asked for.

The program now calculates B_a, $C_{m,a}$, and C_s according to eqs. (2), (3), (4), and (10). Then the optimum conditions can be calculated for a given column (Y = L) or a requested plate number (Y = N). First X = $16\eta Y/r^2$ is calculated, a factor needed in eq. (15) or (22). Next all pressure factors (P, f_1, f_2P, $\bar{p}$) are calculated by a subroutine, using a starting value for the inlet pressure of $p_i = p_o + p_a$.

Based on the value of Y, the program diverts to the appropriate section. If L is given (Y < 1000), ε is calculated from eq. (19). The result is substituted into eq. (15), yielding a new value of p_i. This value of p_i is used as input to the before mentioned subroutine which recalculates all pressure factors.

The results are used to recalculate ε from eq. (19) and subsequently a new value of p_i from eq. (15). In this way the optimum ε is iteratively approached as long as the latest value of p_i differs more than 1 Pa (i.e. 10^{-5} p_a) from its last-but-one value.

Having optimized ε, p_i, and all pressure factors, another subroutine is used to calculate $\bar{u}$ from eq. (9), H from eq. (11), N = L/H, t_R from eq. (47), N/L and N/t_R.

Next the ε from eq. (20) and subsequently ε from eq. (21) are calculated by iteration in exactly the same manner as described for $\varepsilon_{min H}$.

If N is given (Y > 1000), εH is optimized by iteration using eqs. (27) and (22), again by repeatedly using the pressure factor subroutine as described above. This iteration converges slower than those for a given column, especially at elevated outlet pressures. Moreover, the repeated calculations of εH (eq. 27) and p_i (eq. 22) sometimes lead to an infinite loop when the exit criterion is $p_{i,new} - p_{i,last} < 1$ Pa. Therefore, in this case the optimum p_i is approached to within ± 5 Pa. Upon exit, the resulting p_i and pressure factors are substituted in eq. (28) to calculate $\varepsilon_{N,min t}$. The subsequent program flow is the same as described above for L = constant, but using L = NH in the various equations.

Upon completion of the optimization procedures, the H-$\bar{u}$ curve can be computed from eqs. (13) and (14), as described under eq. (14). The H-$\bar{u}$ curve is calculated and printed on request, for inlet pressures in the range of about $\bar{p}_{min H}$ to $2p_{i,min H}$. Finally, one or more of the input data can be changed and the program restarted.

5 Results and Discussion

As an example, the program was used to predict the various optimum conditions for a wide-bore, thick-film SE-30 column, operated with hydrogen carrier gas at atmospheric (Table 1) and vacuum outlet conditions (Table 2).

Table 1

Comparison of calculated and measured optima. Atmospheric outlet conditions.

Table 2

Comparison of calculated and measured optima. Vacuum outlet conditions.

```
INPUT DATA FOR THIS WCOT COLUMN:        MEASURED DATA (COMPUTER FITTED)
                                        HYDROGEN - ATMOSPHERIC OUTLET
L          24.5       m
ID         .53        mm
Df         2.65       um
T          453        K              453   K
k'         2                         2.0
ETA        11.7783    uPa.s          12.8  uPa.s
Dma        38.4       mm^2/s         38.9  mm^2/s   (from Ba)
Ds         .0012      mm^2/s

Ba         76.8       mm^2/s         77.8  mm^2/s
Cma        482.594    us             400   us
Cs         866.975    us             848   us

OPTIMUM CHROMATOGRAPHIC CONDITIONS FOR Po = 100 kPa:

MINIMUM PLATE HEIGHT CONDITIONS FOR THIS COLUMN:  (Eqs. 19 & 11)
(GOLAY - GIDDINGS)

Pi         107.73     kPa            108   kPa
u (average) .235044   m/s            246   mm/s
H          .636287    mm             615   um
t(R)       312.708    s              299   s
N          38504.6                   39848
N/L        1571.62    m^-1
N/t(R)     123.133    s^-1
Pc (GIDDINGS) 29.8791 kPa
Pi/Pc      3.60554
f1         1.00046
f2         .962338
P (average) 103.914   kPa

MINIMUM PLATE HEIGHT CONDITIONS (CRAMERS):  (Eqs. 20 & 11)

Pi         107.735    kPa
u (average) .235182   m/s
H          .636291    mm
t(R)       312.524    s
N          38504.4
N/L        1571.61    m^-1
N/t(R)     123.205    s^-1
Pc (GIDDINGS) 29.879  kPa
Pi/Pc      3.6057
f1         1.00046
f2         .962323
P (average) 103.915   kPa

MINIMUM TIME CONDITIONS FOR THIS COLUMN (LECLERCQ):  (Eqs. 21 & 11)

Pi         137.488    kPa
u (average) 1.131     m/s
H          1.69651    mm
t(R)       64.987     s
N          14441.4
N/L        589.444    m^-1
N/t(R)     222.219    s^-1
Pc (GIDDINGS) 18.2985 kPa
Pi/Pc      7.51364
f1         1.0081
f2         .835213
P (average) 119.73    kPa
```

```
INPUT DATA FOR THIS WCOT COLUMN:        MEASURED DATA (COMPUTER FITTED)
                                        HYDROGEN - VACUUM OUTLET
L          24.5       m
ID         .53        mm
Df         2.65       um
T          453        K              453   K
k'         2                         2.0
ETA        11.7783    uPa.s          12.8  uPa.s
Dma        38.4       mm^2/s         38.9  mm^2/s   (from Ba)
Ds         .0012      mm^2/s

Ba         76.8       mm^2/s         77.8  mm^2/s
Cma        482.594    us             476   us
Cs         866.975    us             793   us

OPTIMUM CHROMATOGRAPHIC CONDITIONS FOR Po = .001 kPa:

MINIMUM PLATE HEIGHT CONDITIONS FOR THIS COLUMN:  (Eqs. 19 & 11)
(GOLAY - GIDDINGS)

Pi         35.3931    kPa            37    kPa
u (average) .807479   m/s            786   mm/s
H          1.25698    mm             1233  um
t(R)       91.0241    s              94    s
N          19491.2                   19875
N/L        795.558    m^-1
N/t(R)     214.132    s^-1
Pc (GIDDINGS) 21.2584 kPa
Pi/Pc      1.6649
f1         1.125
f2         4.23808E-05
P (average) 23.5956   kPa

MINIMUM PLATE HEIGHT CONDITIONS (CRAMERS):  (Eqs. 20 & 11)

Pi         35.3931    kPa
u (average) .807479   m/s
H          1.25698    mm
t(R)       91.0241    s
N          19491.2
N/L        795.558    m^-1
N/t(R)     214.132    s^-1
Pc (GIDDINGS) 21.2584 kPa
Pi/Pc      1.6649
f1         1.125
f2         4.23808E-05
P (average) 23.5956   kPa

MINIMUM TIME CONDITIONS FOR THIS COLUMN (LECLERCQ):  (Eqs. 21 & 11)

Pi         67.4004    kPa
u (average) 1.53772   m/s
H          1.83334    mm
t(R)       47.798     s
N          13363.6
N/L        545.452    m^-1
N/t(R)     279.584    s^-1
Pc (GIDDINGS) 17.6024 kPa
Pi/Pc      3.82904
f1         1.125
f2         2.22551E-05
P (average) 44.9336   kPa
```

The H-$\bar{u}$ curves of this column were measured with n-dodecane as a test compound. The separation temperature of 453 K was tuned to a capacity ratio of k = 2.0 for this solute.

The computer program calculated a good value of the carrier gas viscosity, but the diffusion coefficients were off by about 20%, as expected for this solute [10-12]. Therefore, literature data of the diffusivities [10-12] were entered manually as listed in Table 1.

The experimentally acquired data were fitted to eqs. (1) and (31), for atmospheric and vacuum outlet, respectively [13]. The results from these fits are included in Tables 1 and 2 in the columns "measured".

As can be seen, there is a good agreement between calculated and measured data. Another conclusion is that the approximation of minimum plate-height conditions by Cramers et al. [3] is indeed very good.

Minimum analysis time is achieved only at vacuum outlet operation [5,8]. As a test, the plate number calculated for minimum time conditions with the given 24.5 m column at $p_0 = 0$, (N = 13364), was inputted to the program instead of the column length. The results of the calculations are shown in **Table 3**. The calculated column length is 22.8 m. As expected from the presented theory, and particularly demonstrated for thin-film columns, viz. eqs. (49), (50), and (53), these results define the real minimum time conditions. the values of N/t_R to be compared from Tables 2 and 3 are 279.6 and 281.0 plates per second, respectively. The differences between the minimum retention times for a given column and for a required plate number under similar conditions cannot yet be fully comprehended, however.

Table 4 exemplifies a plate-height curve print-out for the column of Table 2.

Table 3

Calculated minimum time conditions for N = 13364 plates. (cf. Table 2).

```
INPUT DATA FOR THIS WCOT COLUMN:

N        13364
ID        .53        mm
Df       2.65        um
T         453        K
k'          2
ETA     11.7783      uPa.s
Dma     38.4         mm^2/s
Ds       .0012       mm^2/s

Ds       76.8        mm^2/s
Cma    482.594       us
Cs     866.975       us


OPTIMUM CHROMATOGRAPHIC CONDITIONS FOR po = .001 kPa:

MINIMUM TIME CONDITIONS FOR  13364  PLATES   (Eqs. 28 & 11)
(GIDDINGS - LECLERCQ)

Pi         58.7803     kPa
u (average)  1.45979   m/s
H           1.70771    mm
t(R)       47.5522     s
L          22.8218     m
N/L       585.581      m^-1
N/t(R)    281.038      s^-1
Pc (GIDDINGS) 17.6027  kPa
Pi/Pc       3.33928
f1          1.125
f2          2.55208E-05
P (average) 39.1837    kPa
```
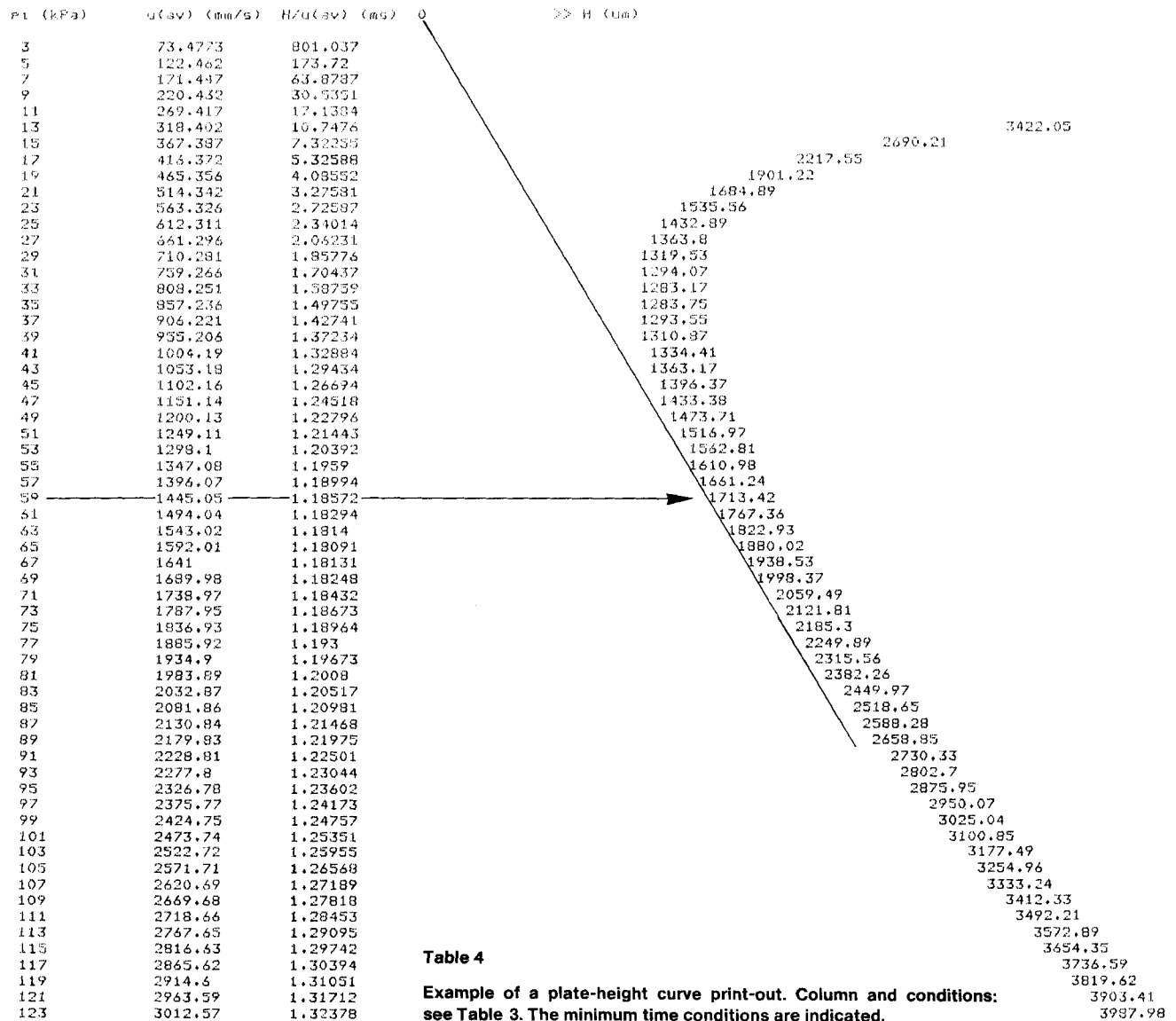
The program and its subroutines were found to be very reliable in numerous calculations. Widely varying input data, and particularly $p_o = 0$ (vacuum outlet) conditions are treated without problems, yielding accurate results. Vacuum outlet data produced by the program (using the general equations) are identical to those obtained by employing the eqs. (32)–(35) and (29) derived for $P \to \infty$.

The good results are produced because the program does not work with extreme values (except in the pressure factor subroutine). In the iterations mostly $f_2 P$, with a value between 1 and 1.5, is employed although f_2 and P might approach zero and infinity, respectively.

Acknowledgment

Pi (kPa)	u(av) (mm/s)	H/u(av) (ms)	0	>> H (um)
3	73.4773	801.037		
5	122.462	173.72		
7	171.447	63.8787		
9	220.432	30.5351		
11	269.417	17.1384		
13	318.402	10.7476		
15	367.387	7.32255		
17	416.372	5.32588		
19	465.356	4.08552		
21	514.342	3.27581		
23	563.326	2.72597		
25	612.311	2.34014		
27	661.296	2.06231		
29	710.281	1.85776		
31	759.266	1.70437		
33	808.251	1.58759		
35	857.236	1.49755		1283.75
37	906.221	1.42741		1293.55
39	955.206	1.37234		1310.87
41	1004.19	1.32884		1334.41
43	1053.18	1.29434		1363.17
45	1102.16	1.26674		1396.37
47	1151.14	1.24518		1433.38
49	1200.13	1.22796		1473.71
51	1249.11	1.21443		1516.97
53	1298.1	1.20392		1562.81
55	1347.08	1.1959		1610.98
57	1396.07	1.18994		1661.24
59	1445.05	1.18572		1713.42
61	1494.04	1.18294		1767.36
63	1543.02	1.1814		1822.93
65	1592.01	1.18091		1880.02
67	1641	1.18131		1938.53
69	1689.98	1.18248		1998.37
71	1738.97	1.18432		2059.49
73	1787.95	1.18673		2121.81
75	1836.93	1.18964		2185.3
77	1885.92	1.193		2249.89
79	1934.9	1.19673		2315.56
81	1983.89	1.2008		2382.26
83	2032.87	1.20517		2449.97
85	2081.86	1.20981		2518.65
87	2130.84	1.21468		2588.28
89	2179.83	1.21975		2658.85
91	2228.81	1.22501		2730.33
93	2277.8	1.23044		2802.7
95	2326.78	1.23602		2875.95
97	2375.77	1.24173		2950.07
99	2424.75	1.24757		3025.04
101	2473.74	1.25351		3100.85
103	2522.72	1.25955		3177.49
105	2571.71	1.26568		3254.96
107	2620.69	1.27189		3333.24
109	2669.68	1.27818		3412.33
111	2718.66	1.28453		3492.21
113	2767.65	1.29095		3572.89
115	2816.63	1.29742		3654.35
117	2865.62	1.30394		3736.59
119	2914.6	1.31051		3819.62
121	2963.59	1.31712		3903.41
123	3012.57	1.32378		3987.98

(Upper H values: 3422.05, 2690.21, 2217.55, 1901.22, 1684.89, 1535.56, 1432.89, 1363.8, 1319.53, 1294.07, 1283.17)

Table 4

Example of a plate-height curve print-out. Column and conditions: see Table 3. The minimum time conditions are indicated.

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Automatic Simulated Distillation of Heavy Petroleum Fractions up to 800°C TBP by Capillary Gas Chromatography
Part I: Possibilities and Limits of the Method

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Summary

The characterization of heavy petroleum fractions is essential for the design and improvement of cracking plants converting heavy feedstock into valuable "white" products. Conventional simulated distillation methods using packed columns are unsuitable for this purposes, being limited to boiling points up to about 600°C. The method presented is able to cover a boiling points interval ranging from about 150°C up to around 800°C. It employs a short, nonpolar, highly thermostable capillary column routinely operated at temperatures around 430°C. The analytical system is based on a high temperature version of a fully automatic, capillary dedicated gas chromatograph. The experimental data demonstrate that cold on-column injection is the sole sampling system suitable for such heavy compounds. The conversion of the retention times into boiling points, based on the use of low molecular weight polyethylenes, is extremely reliable, as demonstrated by the excellent retention time reproducibilities. The lower part (up to 550–600°C TBP) of the boiling point distribution curves of heavy petroleum fractions obtained on capillary columns fits well with the corresponding distribution curves based on packed column data. For the petroleum fractions fully eluted from the column the quantitative results obtained either using internal standards or by direct processing of the elution curves are in excellent agreement (less than 0.3 weight % differences). The method has been applied to the determination of the true boiling points corresponding to short path vacuum distillation (DISTACT) cut points over 300°C.

Dedicated to *Professor Kurt Grob* on his 65th birthday.