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# Optimum Performance of Capillary GC Columns as a Function of Column Diameter and Film Thickness under Various Operating Conditions: Part II: Computer Program Extensions for *n*-Alkane Solutes and Polydimethylsiloxane Phases<sup>1)</sup>

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## Key Words:

Open tubular GC  
Computer-aided optimization  
Detection limits  
Sample capacity

## Summary

A BASIC computer program for calculation of maximum plate number and minimum analysis time conditions for columns operated at various outlet pressures was presented in 1985 [1]. This sequel reports extensions to the program for *n*-alkanes separated on polydimethylsiloxane stationary phases, specifically for *n*-C<sub>2</sub> through *n*-C<sub>20</sub> on phases equivalent to SE-30 or OV-1. For these solute-phase systems the amount of thermodynamic data available is sufficient to enable calculation of several parameters.

Firstly, the separation temperature is now automatically calculated for a requested capacity ratio, or *vice versa*. Secondly, the computation of solute diffusivities in the stationary phase has been improved to approach experimental data more realistically, particularly for higher *n*-alkanes at higher temperatures.

The largest extension to the program is the inclusion of a facility enabling calculation of column sample capacity, minimum detectable amounts for FID and TCD detectors, and column working ranges. These parameters are again calculated for *n*-alkanes, but are, of course, independent of the nature of the stationary phase. The updated program has been and is being used on a routine basis in our laboratory; it has been found to be reliable and has on numerous instances been proven in the field.

## 1 Introduction

Since the publication of some early reports [1, 2], a number of papers on computer-assisted examination and optimization of capillary GC columns has recently appeared [3, 4]. In the latter two reports use is made of the extended *Golay-Giddings* equation, which includes a term for extra-column contributions to the theoretical plate height according to *Gaspar et al.* [5]. This can be a worthwhile addition for computation of optimum conditions for routine GC applications. It is, however, our experience that in a research laboratory extra-column band broadening resulting from injection and detection can be virtually eliminated, even in high-speed applications (with typically more than 20000 plates per second [6, 7]) and we have, therefore, continued to use our program [1] with the unaltered *Golay-Giddings* equation. The

original program has, however, been extended in several other respects, as will be described below.

In general, literature data on solute diffusion coefficients in different stationary phases are scarce. For *n*-alkane solutes, separated on polydimethylsiloxane phases, however, more-or-less reliable thermochemical data are available [8, 9], and these enable the calculation of diffusion coefficients. With these data, moreover, the capacity factor can be calculated from the separation temperature (or *vice versa*) as a function of the phase ratio. This approach differs from that of *Villalobos and Annino* [3], whose program includes an internal table of specific retention volumes for *n*-alkanes and non-polar phases at two temperatures. From these tables their program calculates solute partition ratios at different temperatures, and in this way the capacity factor and/or phase ratio is computed.

The saturated vapor pressures of *n*-alkanes can be calculated by use of the *Antoine* equation. These pressures can then be used to predict column sample capacities (column loadabilities) for these solutes.

## 2 Theory

### 2.1 Capacity Factor and Temperature

The relationship between capacity factor and temperature is given in eq. (1):

$$K = \exp[(\Delta H - T\Delta S) / (R \cdot T)] = k \cdot \beta \quad (1)$$

where *K* is the distribution coefficient of the solute,  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy of evaporation of the solute from the stationary phase, *T* is the absolute temperature, *R* the gas constant (1.987 cal/mole/degree), *k* the capacity factor of the solute, and  $\beta$  the phase ratio:

$$\beta = (r - d_i)^2 / [d_i(2r - d_i)] \approx r / (2d_i) \quad (2)$$

<sup>1)</sup> For Part I see Reference 1.

where  $r$  is the column inner radius, and  $d_f$  the film thickness of the stationary phase. Millen and Hawkes [8] determined the values of  $\Delta S$  and  $\Delta H$  for the evaporation of  $n$ -alkanes from SE-30:

$$\Delta S = R(1.8 + 0.59Z) \text{ [cal/mole/degree]} \quad (3)$$

$$\Delta H = 950 + 905Z \text{ [cal/mole]} \quad (4)$$

where  $Z$  is the carbon number. For  $n$ -alkanes separated on polydimethylsiloxane phases, therefore, the separation temperature,  $T$ , can be calculated from the required capacity factor:

$$T = \Delta H / [\Delta S + R \cdot \ln(k \cdot \beta)] \quad (5)$$

or vice versa, i.e. the capacity factor can be calculated from the given temperature:

$$k = \exp[(\Delta H - T\Delta S) / (R \cdot T)] / \beta \quad (6)$$

## 2.2 Gas/Liquid Diffusion Coefficients

Kong and Hawkes [9] presented an equation for the diffusion coefficient,  $D_s$ , of  $n$ -alkanes in SE-30:

$$\ln(D_s) = -8.87 + 0.3836Z + (446.1 - 498.1Z) / (R \cdot T) \quad (7)$$

$(D_s \text{ in m}^2/\text{s})$

A similar equation was used in our original program [1]:

$$\ln(D_s) = -5 + 0.38Z + (225 - 250Z)/T \quad (8)$$

$(D_s \text{ in mm}^2/\text{s})$

It has been reported that the values of  $D_s$  computed by eq. (7) are too high [8] and Schutjes also found lower  $D_s$  values [6]. We, therefore, have used an adapted equation since 1987:

$$\ln(D_s) = -4.5 + 0.33Z + (225 - 250Z)/T \quad (9)$$

$(D_s \text{ in mm}^2/\text{s})$

## 2.3 Detection limits

The minimum detectable amount is given by eq. (10):

$$Q_{o,m} = \sqrt{(2\pi) \cdot \sigma \cdot 4R_n/S} \text{ [g]} \quad (10)$$

for mass-flow-sensitive detectors (e.g. FID or MS), and eq. (11) for concentration-sensitive detectors (e.g. TCD):

$$Q_{o,c} = \sqrt{(2\pi) \cdot \sigma \cdot F_d \cdot 4R_n/S} \text{ [g]} \quad (11)$$

In these equations  $\sigma$  is the peak width ( $\sigma = t_R/\sqrt{N}$  [s], where  $t_R$  is the solute retention time and  $N$  the corresponding plate number),  $R_n$  and  $S$  are the detector noise and sensitivity, respectively, and  $F_d$ , the flow through the detector (at the pressure and temperature of operation), is given by:

$$F_d = \pi(r - d_f)^2 u_d \text{ [m}^3/\text{s]} \quad (12)$$

with  $u_d$  denoting the linear gas velocity through the detector. In the absence of make-up gas or eluate splitting, the detector flow is equal to the column flow ( $F_d = F_c$  and  $u_d = u_o$ , the linear velocity at the column outlet). If the detector is operated at the same temperature as the column:

$$u_d = u_o = \bar{u} \cdot \bar{p} / p_d \text{ [m/s]} \quad (13)$$

where  $\bar{u}$  and  $\bar{p}$  represent the average gas velocity and pressure, respectively, and  $p_d$  is the pressure in the detector.

## 2.4 Sample Capacity

The maximum loadability of a GC column is given by [10]:

$$Q_s = C\sqrt{K_i\pi}(r - d_f)^2\sqrt{(L \cdot H)(1 + k)p_s M/(R \cdot T)} \quad (14)$$

where  $L$  is the column length,  $H$  the plate height ( $L = N \cdot H$ ), and  $p_s$  and  $M$  are, respectively, the saturated vapor pressure and molecular mass ([g/mole]) of the solute.  $K_i$  is the injection profile factor, and has a value of 12 for plug injections. The constant  $C$  is determined by the ratio [injection bandwidth]: [bandwidth obtained from the chromatographic column alone]. If a 10% reduction of the plate number (which is 5% reduction in resolution) can be tolerated, this corresponds to an injection band width of about 50% of the bandwidth obtained from the separation process. Under these conditions, the constants  $C\sqrt{K_i\pi}$  in eq. (14) thus combine to produce  $\pi\sqrt{3}$ .

The saturated vapor pressure can be calculated by the Antoine equation:

$$\log(p_s) = A - B/(C + T) \quad (15)$$

## 3 Results and Discussion

Measured and calculated gas/liquid diffusion coefficients are compared in **Table 1**. It is apparent that eq. (9) (new program) fits Schutjes data [6] much better than eq. (8) (old program).

**Table 1**

**Diffusion coefficient ( $D_s \times 10^{-9} \text{ m}^2/\text{s}$ ) for  $n$ -alkanes  $C_2H_{2z+2}$  in SE-30.**

T [K]	Z	Measured		Calculated	
		Ref. 8	Ref. 6	Eq. (8)	Eq. (9)
373	8	1.25		1.21	1.33
	9	1.15		0.90	0.95
	10	0.94	0.59–0.72	0.68	0.68
	11	0.80	0.43–0.51	0.51	0.48
	12	0.54	0.28–0.38	0.38	0.34
423	11	1.79	0.95–1.06	1.13	1.07
	12	1.48	0.84–0.94	0.91	0.82
	13	1.22	0.70–0.86	0.74	0.64
	14	0.96	0.45–0.58	0.60	0.49
	15		0.29–0.39	0.48	0.38
	16	0.58	0.18–0.27	0.39	0.29
473	16	1.67		1.01	0.75
	17		0.43–0.70	0.87	0.61
	18	1.20	0.33–0.54	0.75	0.50
	19		0.25–0.48	0.65	0.41
	20		0.18–0.43	0.56	0.34

For the  $C_2$ - $C_{20}$   $n$ -alkanes, the constants from the Antoine equation (eq. (15)) were fitted to the constants for the individual alkanes, as published by the API44-TRC project [11]. Accurate values for the saturated vapor pressures of these  $n$ -alkanes were obtained by using the "constants" in **Table 2** (with  $p_s$  expressed in mm Hg):

**Table 2**

**Antoine "constants" ( $X$ ) as a function of the carbon number ( $Z$ ) of  $n$ -alkanes:  $X = a + bZ + cZ^2$ .**

"Constant"	a	b	c
A	6.7	0.0336	-0.0008
B	416.5	142.5	-3.36
C	0.69	-8.78	0.085

## INPUT DATA FOR THIS WCOT COLUMN:

COLUMN LENGTH	7.5	25	m
INNER DIAMETER	50	320	$\mu\text{m}$
FILM THICKNESS	.08	.52	$\mu\text{m}$
CARRIER GAS	HELIUM	HELIUM	
STATIONARY PHASE	SE-30	SE-30	
n-ALKANE	C- 10	C- 10	
CAPACITY FACTOR	2.81	2.76	
TEMPERATURE	365.0532	365.9407	K
DYN. VISCOSITY	22.43261	22.46783	$\mu\text{Pa}\cdot\text{s}$
BIN. GAS DIFFUSION	28.58833	28.71009	$\text{mm}^2/\text{s}$
GAS/LIQ. DIFFUSION	.5920214	.6010371	$\times 10^{-3} \text{mm}^2/\text{s}$
B-TERM (at 100 kPa)	57.17666	57.42017	$\text{mm}^2/\text{s}$
Cm-TERM (at 100 kPa)	6.571244	266.3531	$\mu\text{s}$
Cs-TERM	1.395108	58.55278	$\mu\text{s}$

## OPTIMUM CHROMATOGRAPHIC CONDITIONS FOR 100 kPa OUTLET PRESSURE:

## MINIMUM PLATE HEIGHT CONDITIONS FOR THIS COLUMN (GOLAY-GIDDINGS):

INLET PRESSURE (absolute)	1132.09	158.8828	kPa
GAS VELOCITY (average)	388.4075	329.7703	$\text{mm}/\text{s}$
RETENTION TIME	73.56965	285.0469	s
PLATE HEIGHT	43.87487	271.5058	$\mu\text{m}$
PLATE NUMBER	170940.7	92079.07	
PLATES PER LENGTH UNIT	22792.09	3683.163	$\text{m}^{-1}$
PLATES PER TIME UNIT	2323.522	323.0313	$\text{s}^{-1}$
DETECTION LIMIT (FID)	.8897047	4.696841	pg
DETECTION LIMIT (TCD)	21.80643	691.7313	pg
SAMPLE CAPACITY	3.644087	692.7372	ng (10% peak broadening)
WORKING RANGE (FID)	4095.839	147490	
WORKING RANGE (TCD)	167.1107	1001.454	

## MINIMUM PLATE HEIGHT CONDITIONS (CRAMERS):

INLET PRESSURE (absolute)	1135.382	159.778	kPa
GAS VELOCITY (average)	389.5639	334.651	$\text{mm}/\text{s}$
RETENTION TIME	73.35023	280.8896	s
PLATE HEIGHT	43.87562	271.5514	$\mu\text{m}$
PLATE NUMBER	170937.8	92063.6	
PLATES PER LENGTH UNIT	22791.7	3682.544	$\text{m}^{-1}$
PLATES PER TIME UNIT	2330.433	327.7572	$\text{s}^{-1}$
DETECTION LIMIT (FID)	.8870589	4.628729	pg
DETECTION LIMIT (TCD)	21.8692	694.4575	pg
SAMPLE CAPACITY	3.644119	692.7955	ng (10% peak broadening)
WORKING RANGE (FID)	4108.091	149672.9	
WORKING RANGE (TCD)	166.6325	997.6066	

## MINIMUM TIME CONDITIONS FOR THIS COLUMN (LECLERCQ):

INLET PRESSURE (absolute)	1499.176	215.8536	kPa
GAS VELOCITY (average)	517.6317	631.6886	$\text{mm}/\text{s}$
RETENTION TIME	55.20335	148.8075	s
PLATE HEIGHT	50.97516	379.7485	$\mu\text{m}$
PLATE NUMBER	147130.5	65833.05	
PLATES PER LENGTH UNIT	19617.4	2633.322	$\text{m}^{-1}$
PLATES PER TIME UNIT	2665.246	442.4041	$\text{s}^{-1}$
DETECTION LIMIT (FID)	.7195883	2.899832	pg
DETECTION LIMIT (TCD)	31.03354	1025.2	pg
SAMPLE CAPACITY	3.927898	819.2697	ng (10% peak broadening)
WORKING RANGE (FID)	5458.535	282523.2	
WORKING RANGE (TCD)	126.5694	799.1318	

Figure 1

Examples of program output for two different columns.

The computer program asks for the following input data:  $L$  or  $N$ ;  $r$ ,  $d_i$ ,  $Z$ ,  $T$ , or  $k$ ; type of carrier gas, and outlet pressure. It then calculates the various optimum conditions completely automatically for  $n$ -alkanes on phases of the type SE-30 or OV-1.

As output,  $p_i$ ,  $t_R$ ,  $H$ ,  $N$  (or  $L$ ),  $N/L$ ,  $N/t_R$ , detection limits, sample capacity, and column working range ( $Q_s/Q_o$ ) are provided for minimum time, minimum plate height ( $L$  given), or minimum column length ( $N$  given) conditions. A description of the algorithms is given in reference 1; only the program extensions will be discussed here.

After asking for values of  $k$  or  $T$ , the program considers values lower than 100 to be capacity factors, and those higher than 100 to be separation temperatures [K]. Using eqs (3) and (4), eqs (5) or (6) are computed depending on the value entered.

After calculation of  $p_s$  from eq. (15) with the constants from Table 2, and using  $M = 14Z + 2$  [g/mole], the sample capacity is computed according to eq. (14). For calculation of the detection limits, detector sensitivities and noise are assumed to have the values listed in **Table 3**.

**Table 3**

**Detector sensitivity and noise.**

Detector	Sensitivity	Noise
FID (or MS)	$S = 10^{-2}$ As/g	$R_n = 5 \times 10^{-15}$ A
TCD [12]	$S = 250T/(Mp_d)$ Vm <sup>3</sup> /g	$R_n = 5 \times 10^{-6}$ V

Substitution of the data from Table 3 into eqs (10) and (11), and using eq. (13), yields:

$$Q_{o,m} \approx 5 \times 10^{-12} \cdot \sigma [g] \text{ and } Q_{o,c} \approx 5 \times 10^{-7} \cdot \sigma(r - d_i)^2 \cdot \bar{v} \cdot \bar{p} \cdot M/T [g]$$

for mass-flow- and concentration-dependent detectors, respectively. The program calculates  $Q_{o,c}$  from  $Q_{o,c} = 10^5 \cdot Q_{o,m}(r - d_i)^2 \cdot \bar{v} \bar{p} M/T$

An example of the updated program output is presented in **Figure 1**. Noy *et al.* [13] measured the minimum detectable amounts on these two particular columns. Taking into account their values for coating efficiencies, and a higher FID noise level, the calculated data agree very well with the experimental results. The calculated column loadabilities and TCD data are also comparable with experimental findings [10, 12].

## Corrections

Several printing errors appear in the previous publication on the original computer program [1]. The term  $(f_1 - f_2 \cdot P)$  in eq. (17) should read  $(2f_1 - f_2 \cdot P)$ . In the line following eq. (18),  $0 < P < \infty$  must be replaced by  $1 < P < \infty$ .  $\delta(H/\bar{p})$  in eq. (24) should be  $\delta(H/\bar{v})$ , and  $C_s$  in eq. (32) should be  $2C_s$ .

Quite a few copies of the computer program have been freely distributed. Early users are notified that in the versions of the program prior to that of April 1987, there was an error in lines 2250 and 2260, where M should be replaced by M1.

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