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## OPTIMIZATION OF BASIC PARAMETERS IN TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHIC SEPARATIONS OF MULTI-COMPONENT SAMPLES WITHIN A GIVEN TIME

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### SUMMARY

A new procedure is introduced for the optimization of column peak capacity in a given time. The optimization focuses on temperature-programmed operating conditions, notably the initial temperature and hold time, and the programming rate. Based conceptually upon Lagrange functions, experiments were carried out along simplex sequential and central composite design procedures. The validity of the theory was demonstrated by separations of some crude oil distillation fractions.

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### INTRODUCTION

The separation of complex mixtures in capillary gas chromatography (GC) can be improved by the optimization of a combination of column selectivity and/or efficiency and/or analysis time. The approach to this optimization will greatly depend upon the number of components present in the sample, and upon the differences in polarity and volatility of the sample constituents.

Optimization of the column temperature in isothermal and temperature-programmed operation has been studied by many authors<sup>1–15</sup>. Simplex sequential methods have been applied for the optimization of the initial temperature and temperature gradient<sup>5–8</sup>. A different approach, called “experimental design”, was used for the optimization of the temperature gradient and carrier gas velocity<sup>9,10</sup>. In some recent publications, isothermal retention data were used for the optimization of multi-ramp temperature-programmed GC separations<sup>11–15</sup>. Recently, reports appeared on selectivity optimization in isothermal capillary GC, by tuning the column temperature(s) in series-coupled capillary columns in single- or dual-oven GC systems<sup>16,17</sup>. In all of these studies, optimization of the initial isothermal hold time was not included.

In this paper the optimization of the peak capacity in temperature-programmed capillary GC in a given time is discussed. This optimization is performed by tuning the initial temperature and hold time, as well as the programming rate in a single-oven GC instrument. The theory is outlined, and its applicability is demonstrated by separations of aliphatic and aromatic crude oil distillation fractions.

## THEORETICAL

### *Optimization criteria*

For the exploitation of statistical optimization methods in chromatography, proper criteria are required. Unfortunately, all criteria dealt with up till now<sup>18,19</sup> fail whenever the number of peaks in the chromatogram is not constant during optimization.

For multi-component samples, with more than a few hundred components, optimization of the peak capacity according to Grushka<sup>20</sup> can give a significant improvement of the separation. The peak capacity (PC) can be calculated in isothermal as well as temperature-programmed separations<sup>21</sup> from

$$PC = 1.18 \sum_{i=m}^{n-1} (TZ_i + 1) \quad (1)$$

where  $TZ_i$  is the "Trennzahl" or separation number<sup>21</sup> for the  $i$ th pair of adjacent  $n$ -alkanes, and  $m$  and  $n$  are the lowest and highest carbon numbers, respectively, of the  $n$ -alkanes in the range considered.

The position of any peak in temperature-programmed GC will depend upon the initial temperature,  $T_0$ , and hold time,  $t_0$ , and the programming rate,  $r$ . Therefore, optimization of the peak capacity within a given time can be realized by simultaneous tuning of these parameters.

### *Fundamental approach*

A Lagrange function,  $F$  (ref. 22), was used for the optimization, so that a time constraint can be included

$$F = PC - \lambda(t_{R,n} - t_{R,n,max}) \quad (2)$$

where  $\lambda$  = Lagrange multiplier,  $t_{R,n}$  = retention time of the last eluting  $n$ -alkane of interest and  $t_{R,n,max}$  = the required or maximum analysis time.

Because both PC and  $t_{R,n}$  are functions of  $T_0$ ,  $t_0$  and  $r$ , the Lagrange function  $F = F(T_0, t_0, r, \lambda, t_{R,n,max})$ . For optimum separation conditions (maximum PC in a given analysis time),  $F$  should be maximized. Hence, the partial derivatives of  $F$  should be equal to zero:

$$\partial F(T_0, t_0, r, \lambda) / \partial T_0 = 0 \quad (3a)$$

$$\partial F(T_0, t_0, r, \lambda) / \partial t_0 = 0 \quad (3b)$$

$$\partial F(T_0, t_0, r, \lambda) / \partial r = 0 \quad (3c)$$

$$\partial F(T_0, t_0, r, \lambda) / \partial \lambda = 0 \quad (3d)$$

## EXPERIMENTAL

A 4180 gas chromatograph (Carlo Erba, Milan, Italy) with a Grob-type cold on-column injection port and flame ionization detection (FID) was used. The oven temperature was controlled by a temperature programmer LT 410 (Carlo Erba). Retention times and half height peak widths were measured by a computing integrator C-R3A (Shimadzu, Kyoto, Japan).

The capillary column was made of soft soda-lime glass (91 m  $\times$  0.3 mm I.D.). The inner wall of the column was etched with gaseous hydrogen chloride at 330°C during 24 h. The stationary phase was coated statically, using a 1% solution of SE-30 in dichloromethane. Hydrogen was used as the carrier gas at constant inlet pressure; the linear gas velocity was 25 cm/s at 80°C. All calculations were performed on an HP-85B microcomputer connected to a HP 9121 disc drive. A matrix ROM, advanced programming ROM and printer/plotter ROM were used additionally (all from Hewlett-Packard, Palo Alto, CA, U.S.A.).

A model mixture was prepared by mixing C<sub>8</sub>–C<sub>14</sub> *n*-alkanes in dichloromethane (10 ng/ $\mu$ l per component). A sample of light petroleum was dissolved in dichloromethane (1  $\mu$ g/ $\mu$ l). Aromatic hydrocarbons were isolated from the light petroleum by column liquid chromatography on silica, and successively diluted in dichloromethane (1  $\mu$ g/ $\mu$ l)<sup>23</sup>.

In all cases 1  $\mu$ l was injected into the column.

## RESULTS AND DISCUSSION

Assuming a time constraint of 120 min (=  $t_{R,n,max}$ ), a simplex sequential approach was selected for the optimization of the peak capacity for a crude oil distillation fraction, ranging from *n*-octane (*n*-C<sub>8</sub>) to *n*-tetradecane (*n*-C<sub>14</sub>). The range of parameter values to be optimized was chosen between 40 and 230°C for the initial temperature,  $T_0$ , 0–120 min for the initial hold time,  $t_0$ , and 0–20°C/min for the programming rate,  $r$ . The corresponding interval steps were 1°C, 1 min and 0.1°C/min, respectively.

The results of this approach are summarized in Table I, where peak capacities calculated from eqn. 1 and measured tetradecane retention times are given for the operating conditions resulting from the simplex procedure. In cases where the time constraint was not met, no retention times or peak capacities for *n*-C<sub>14</sub> are given. Obviously, the region of maximum peak capacity within a maximum acceptable retention time is reached at experiment 28.

The dependence of the column peak capacity (PC) and the analysis time,  $t_{R,n}$ , upon the initial temperature, the time of the initial isothermal temperature and the temperature gradient is described by the following set of quadratic equations<sup>22</sup>:

$$PC = a_0 + a_1T_0 + a_2r + a_3t_0 + a_{1,1}T_0^2 + a_{2,2}r^2 + a_{3,3}t_0^2 + a_{1,2}T_0r + a_{1,3}T_0t_0 + a_{2,3}rt_0 \quad (4)$$

$$t_{R,n} = b_0 + b_1T_0 + b_2r + b_3t_0 + b_{1,1}T_0^2 + b_{2,2}r^2 + b_{3,3}t_0^2 + b_{1,2}T_0r + b_{1,3}T_0t_0 + b_{2,3}rt_0 \quad (5)$$

TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS IN THE COURSE OF THE SIMPLEX SEQUENTIAL OPTIMIZATION

<i>Exp. No.</i>	$T_0$ ( $^{\circ}\text{C}$ )	$r$ ( $^{\circ}\text{C}/\text{min}$ )	$t_0$ ( <i>min</i> )	<i>PC</i>	$t_{R,n}$ ( <i>min</i> )
1	80	3.0	10	232	52.9
2	90	3.0	10	217	49.6
3	80	5.0	10	198	41.4
4	80	3.0	20	251	62.8
5	87	1.0	17	286	97.0
6	92	0.1	22	—	—
7	74	1.7	21	289	86.3
8	63	0.7	30	—	—
9	81	0.8	29	—	—
10	80	2.2	16	260	68.3
11	81	0.3	16	—	—
12	80	2.0	19	272	74.5
13	81	0.9	21	300	112.9
14	81	0.1	25	—	—
15	81	0.3	21	—	—
16	80	1.4	19	281	88.2
17	81	0.9	20	308	111.9
18	81	0.5	20	—	—
19	71	1.3	25	307	105.2
20	80	0.5	23	—	—
21	76	1.2	22	306	107.6
22	71	1.4	23	300	99.4
23	77	1.1	22	308	106.5
24	76	1.0	23	311	113.9
25	75	0.8	23	—	—
26	85	0.7	18	312	120.0
27	96	0.2	13	—	—
28	78	0.9	22	323	117.4
29	77	0.9	23	318	119.3
30	83	0.6	20	—	—
31	79	0.9	21	306	115.3

The coefficients of these equations were calculated by multiple linear regression analysis. The experimental conditions for this approach, which are given in Table II, were selected by a central composite design around the optimum found by the simplex procedure<sup>22</sup>.

Differences in peak capacity under similar experimental conditions, for instance experiment 28 in Table I and experiment 9 in Table II, are not only caused by random variations in experimental conditions, *e.g.*, column temperatures or temperature programs, etc. or measurements (peak widths, etc.), but also by column ageing. (The data from Table II were acquired several months after collecting the data in Table I.) The reliability of the *PC* values in both tables corresponds to a standard deviation of about four units. However, the *PC* values in Table II are systematically lower than those in Table I.

TABLE II

EXPERIMENTAL CONDITIONS AND RESULTS OF THE CENTRAL COMPOSITE DESIGN AROUND THE OPTIMUM DERIVED BY THE SIMPLEX STRATEGY

Exp. No.	$T_0$ ( $^{\circ}\text{C}$ )	$r$ ( $^{\circ}\text{C}/\text{min}$ )	$t_0$ (min)	PC	$t_{R,n}$ (min)
1	74	0.6	18	342	136.1
2	82	0.6	18	319	135.6
3	74	1.1	18	308	105.3
4	82	1.1	18	302	98.0
5	74	0.6	26	349	157.4
6	82	0.6	26	319	143.0
7	74	1.1	26	320	113.3
3	82	1.1	26	313	105.8
9	78	0.9	22	307	116.8
10	83	0.9	22	305	111.3
11	73	0.9	22	324	122.5
12	78	1.2	22	302	100.7
13	78	0.6	22	324	145.4
14	78	0.9	27	314	121.0
15	78	0.9	17	318	112.1

Requiring an analysis time of 120 min, the Lagrange function, eqn. 2, can be expressed as

$$\begin{aligned}
 F = & a_0 + a_1 T_0 + a_2 r + a_3 t_0 + a_{1,1} T_0^2 + a_{2,2} r^2 + a_{3,3} t_0^2 + a_{1,2} T_0 r + \\
 & + a_{1,3} T_0 t_0 + a_{2,3} r t_0 - \lambda (b_0 + b_1 T_0 + b_2 r + b_3 t_0 + b_{1,1} T_0^2 + \\
 & + b_{2,2} r^2 + b_{3,3} t_0^2 + b_{1,2} T_0 r + b_{1,3} T_0 t_0 + b_{2,3} r t_0 - 120) \quad (6)
 \end{aligned}$$

where use was made of eqns. 4 and 5. It also follows from eqns. 3, that the parameters  $T_0$ ,  $t_0$ ,  $r$  and  $\lambda$ , corresponding to the maximum value of the column peak capacity in an analysis time of 120 min must be fitted by the following equations:

$$\begin{aligned}
 \partial F / \partial T_0 = & a_1 + 2a_{1,1} T_0 + a_{1,2} r + a_{1,3} t_0 - \lambda (b_1 + 2b_{1,1} T_0 + \\
 & + b_{1,2} r + b_{1,3} t_0) = 0 \quad (7a)
 \end{aligned}$$

$$\begin{aligned}
 \partial F / \partial t_0 = & a_3 + 2a_{3,3} t_0 + a_{1,3} T_0 + a_{2,3} r - \lambda (b_3 + 2b_{3,3} t_0 + \\
 & + b_{1,3} T_0 + b_{2,3} r) = 0 \quad (7b)
 \end{aligned}$$

$$\begin{aligned}
 \partial F / \partial r = & a_2 + 2a_{2,2} r + a_{1,2} T_0 + a_{2,3} t_0 - \lambda (b_2 + 2b_{2,2} r + \\
 & + b_{1,2} T_0 + b_{2,3} t_0) = 0 \quad (7c)
 \end{aligned}$$

$$\begin{aligned} \partial F/\partial \lambda = & -(b_0 + b_1 T_0 + b_2 r + b_3 t_0 + b_{1,1} T_0^2 + b_{2,2} r^2 + b_{3,3} t_0^2 + \\ & + b_{1,2} T_0 r + b_{1,3} T_0 t_0 + b_{2,3} r t_0 - 120) = 0 \quad (7d) \end{aligned}$$

Substituting the  $a$  and  $b$  coefficients as computed before, these non-linear equations were solved numerically by a Newton method<sup>24</sup>. Due to random experimental errors, causing noisy response surfaces for the optimum operating conditions and the calculated peak capacity, more than one solution can be obtained by this numerical approach. In this particular case, two optima were observed, corresponding to the optimum parameters as shown in Table III. The peak capacities in Table III were calculated with eqn. 4.

TABLE III

MAXIMUM PEAK CAPACITIES AND THE CORRESPONDING OPTIMUM EXPERIMENTAL PARAMETERS FOR A REQUIRED ANALYSIS TIME OF 120 min

Determined by solving the Lagrange function.

PC	$T_0$ ( $^{\circ}\text{C}$ )	$t_0$ (min)	$r$ ( $^{\circ}\text{C}/\text{min}$ )	$\lambda$
306	81.7	22.3	0.82	0.332
316	71.9	14.5	2.05	0.549

The optimized separation of a crude oil distillation fraction is shown in Fig. 1. The first set of optimum conditions in Table III was used. The retention time of tetradecane,  $t_{R,n} = 119.7$  min, matches the required analysis time very well.

A chromatogram under identical conditions of the aromatic fraction of this sample, after removal of the saturated hydrocarbons by liquid-solid chromatography

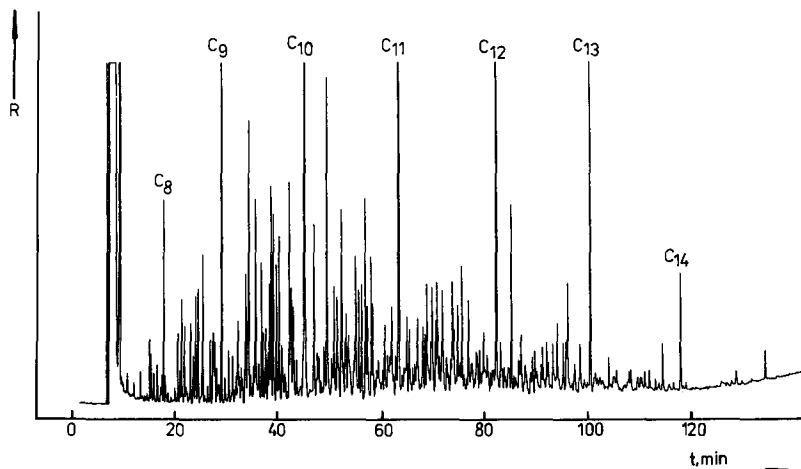


Fig. 1. Chromatogram of a crude oil distillation fraction at optimum temperature-programmed operating conditions. Time constraint 120 min.

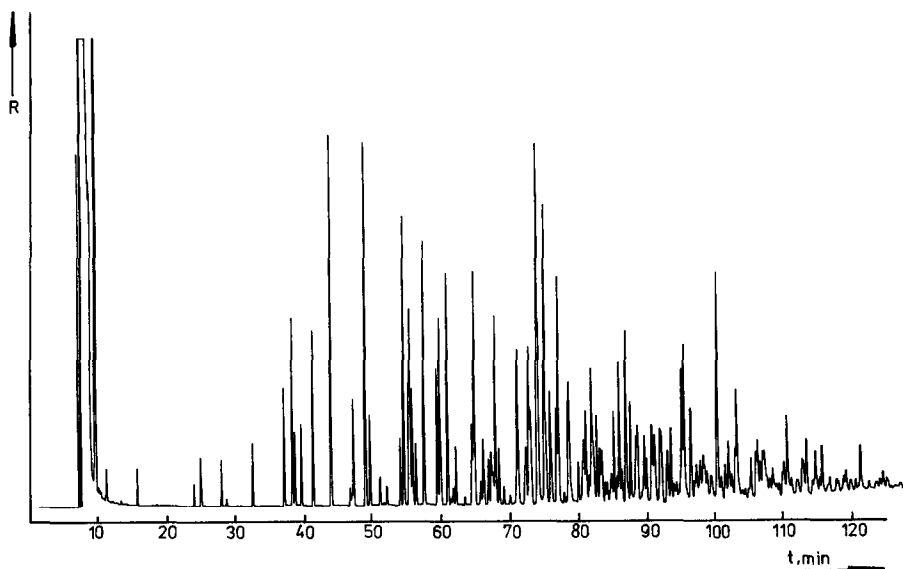


Fig. 2. Chromatogram of the aromatic fraction of the crude oil distillation fraction of Fig. 1.

(*cf.*, Experimental), is given in Fig. 2. Obviously, the number of peaks in the sample considerably exceeds the maximum peak capacity. When the saturated alkanes are removed off-line, prior to GC separation, the approach would be expected to be more efficient, if the optimization had been tuned to the range  $n\text{-C}_9$  through  $n\text{-C}_{14}$ . With the latter sample much better results are expected with a more selective stationary phase for aromatics with the same procedure.

## CONCLUSIONS

Simplex optimization of the peak capacity within a given analysis time can be used for a first approximation. Fine tuning by a (14-point) central composite design around this optimum yields the conditions for (at least 10) experiments, needed to compute the 20 coefficients of the Lagrange function used. After insertion of the required analysis time, this function can then be solved numerically to yield the experimental conditions leading to the maximum peak capacity in the given time. From the experimental results of this particular study, it is not evident that the Lagrange method yields better results than the simplex method. Whether it is necessary to apply a simplex procedure prior to a central composite design is a subject of further investigation.

## REFERENCES

- 1 D. W. Grant and M. G. Hollis, *J. Chromatogr.*, 158 (1978) 3.
- 2 L. A. Jones, S. L. Kirby, C. L. Garganta, T. M. Gerig and J. D. Mulik, *Anal. Chem.*, 55 (1983) 1354.
- 3 N. W. Davies, *Anal. Chem.*, 56 (1984) 2600.
- 4 E. M. Sibley, C. Eon and B. L. Karger, *J. Chromatogr. Sci.*, 11 (1973) 309.

- 5 J. Holderith, T. Toth and A. Váradi, *Magy. Kem. Foly.*, 81 (1975) 162.
- 6 J. Holderith, T. Tóth and A. Váradi, *J. Chromatogr.*, 119 (1976) 215.
- 7 M. Šingliar and L. Koudelka, *Chem. Prum.*, 29 (1979) 134.
- 8 F. H. Walters and S. N. Deming, *Anal. Lett.*, 17 (1984) 2197.
- 9 J. P. Zajcev and V. A. Zazhigalov, *Tezisy Dokl. Ukr. Resp. Kont. Fiz. Khim.*, 12 (1977) 175; *C.A.*, 92 (1978) 208 545 p.
- 10 W. Witkowski and J. Lütke, *Chem. Technol.*, 35 (1983) 419.
- 11 V. Bártů and S. Wičar, *Anal. Chim. Acta*, 150 (1983) 245.
- 12 V. Bártů, S. Wičar, G.-J. Scherpenzeel and P. A. Leclercq, *J. Chromatogr.*, 370 (1986) 219.
- 13 V. Bártů, S. Wičar, G.-J. Scherpenzeel and P. A. Leclercq, *J. Chromatogr.*, 370 (1986) 235.
- 14 Lu Peichang, Lin Bingcheng, Chu Xinhua, Luo Chunroq, Lai Guangda and Li Haochun, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 702.
- 15 H.-J. Stan and B. Steinbach, *J. Chromatogr.*, 290 (1984) 311.
- 16 J. Krupčík, J. Garaj, P. Čellar and G. Guiochon, *J. Chromatogr.*, 312 (1984) 1.
- 17 D. Repka, J. Krupčík, E. Benická, P. A. Leclercq and J. A. Rijks, *J. Chromatogr.*, 463 (1989) 243.
- 18 H. J. G. Debets, B. L. Bajema and D. A. Doornbos, *Anal. Chim. Acta*, 151 (1983) 131.
- 19 P. J. Schoenmakers, *Optimization of Chromatographic Selectivity*, Elsevier, Amsterdam, 1986.
- 20 E. Grushka, *Anal. Chem.*, 42 (1970) 1142.
- 21 J. Krupčík, J. Garaj, G. Guiochon and J. M. Schmitter, *Chromatographia*, 14 (1981) 501.
- 22 G. S. G. Beveridge and R. S. Schetter, *Optimization, Theory and Practice*, McGraw-Hill, New York, 1970.
- 23 Z. Hricová-Nayová, *Graduation thesis*, Technical University of Bratislava, Bratislava, 1984.
- 24 M. Kubíček, *Numerical Algorithms for Solving Chemical Engineering Problems* (in Czech), State Publishing Company of Technical Literature/ALFA, Prague, 1983.