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Computer-assisted optimization of two-factor selectivity in gas chromatography using an advanced simplex method

QIN-SUN WANG*, CHANG-SHOU ZHU and BING-WEN YAN
National Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071 (China)
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ABSTRACT

A computer-assisted simplex method is presented for the optimization of two-factor (carrier gas flow-rate and column temperature) selectivity for the optimum separation of ten compounds in gas chromatography. A two-factor selectivity rectangle concept was used. The method is based on a special polynomial estimated from nine preliminary experimental runs, using the resolution as the selection criterion, with connection to a general simplex method for optimization selection using a microcomputer. Excellent agreement was obtained between predicted data and experimental results, and more than half the number of experiments required in the general simplex method can be omitted.

INTRODUCTION

Studies of systematic strategies for the optimization of gas chromatography (GC) have demostrated the great potential of this approach for improving separations. The sequential simplex method[1,2], response surface method[3], window diagrams[4–7] and computer-simulation techniques[8–10] have been suggested as methods for the optimization of stationary phase loading, column temperature and carrier gas flow-rate selectivity in GC. In most of the previously published papers only one factor was optimized in GC, apart from the simplex method. With optimization of a single factor often the results are not as good as might be expected from a optimum separation. Sometimes a multi-factor optimization can give a completely optimized separation. However, with the sequential simplex method a larger number of experiments are required and local optima may be found, which are distinct disadvantages.

In this paper, a computer-assisted simplex method is presented for the optimization of two-factor (carrier gas flow-rate and column temperature) selectivity for the optimum separation of a mixture of ten compounds in GC. The principle of method is based a special polynomial between the capacity factor, k', and two factors which are estimated from nine preliminary experiments according to the full factorial design, followed by the general simplex method. Excellent agreement was obtained

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between predicted and experimental results and, compared with the original simplex method, more than half the number of experiments can be omitted. For the optimization the computer program SDO-G (simplex difactor optimization for GC) was developed.

EXPERIMENTAL

Materials

The sample contained equal volumes of ten compounds diluted 1:100 in acetone: isoamyl acetate, dodecane, chlorobenzene, 1,3,5-trimethylbenzene,*o*-chlorotoluene, bromobenzene, *m*-dichlorobenzene, *o*-dichlorobenzene, diethyl malonate and 1,4-butyrolactone. These components were eluted in the above order under every set of experimental conditions.

Stainless-steel columns (1 m × 2 mm I.D.) packed with 10% polyethylene glycol 20000 on Chromosorb (80–100 mesh) were used.

Apparatus

All computer studies were carried out on a Model IBM-XT personal computer system with an HP-7470A graphics plotter (Hewlett-Packard, Palo, Alto, CA, U.S.A.). The SDO-G program was written in True BASIC language. An HP-5890A gas chromatograph equipped with flame ionization detectors was employed. The carrier gas was nitrogen. A 10-μl syringe was used for all sample injections.

Chromatography

During the chromatographic runs, all experimental variables except those being investigated were carefully maintained at fixed values. Those variables held constant included the detector air and hydrogen flow-rates, the detector and injection port temperatures (235 and 240°C, respectively) and the sample size (2 μl). The effects of carrier gas flow-rate and column oven temperature were assessed using a full 3^2 factorial design. The flow-rate levels in the design were 10, 20 and 30 ml/min and the temperature levels were 150, 165 and 180°C. The retention time of acetone was employed as t_0.

RESULTS AND DISCUSSION

The principle of the computer-assisted simplex method is based a special polynomial between capacity factor and the two factors considered. In order to investigate the effect of two variables (carrier gas flow-rate and column temperature) in GC and their possible interaction, a full factorial design (Fig. 1) was adopted as the optimization strategy. Nine preliminary experiments were carried out and the capacity factor values were measured. These values were then substituted into the following equation, in order to establish the values of the constants:

$$k' = b_0 + b_1 \log X_1 + b_2 \log X_2 + b_{11} (\log X_1)^2 + b_{22} (\log X_2)^2 + b_{12} \log X_1 \log X_2 \quad (1)$$

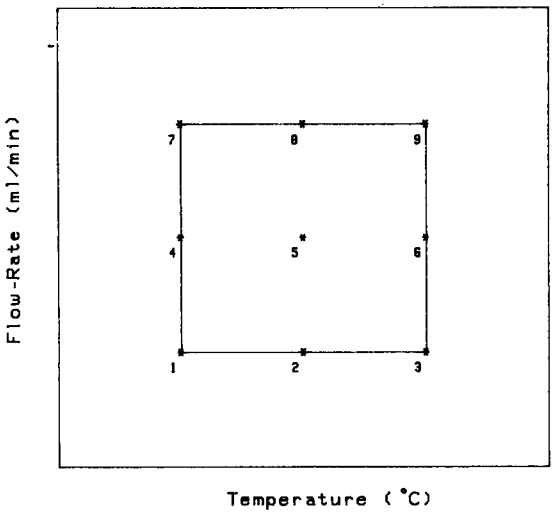

Fig. 1. Full factorial design for two-factor effects.

where X_1 is the carrier gas flow-rate, X_2 is the column temperature and b_0, b_1, b_2, b_{11}, b_{22} and b_{12} are constants characteristic of a given compound. Eqn. 1 means that if X_1 and X_2 are known the capacity factor can be determined for the chromatographic conditions applied.

As the SDO-G method considers only two factors, only three initial experiments were required, which can be selected from the nine preliminary experiments to perform the simplex process and obtain the maximum resolution (R_s). The analysis time can be controlled to limit the k' value.

Resolution is used as a criterion of separation, which can be affected by three independent factors:

$$R_s = \frac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\sqrt{N}\left(\frac{k'}{1 + k'}\right) \tag{2}$$

where α is the selectivity factor for two peaks and N is the column plate number.

Note that the predicted k' values are used to arrange the solutes in order, then calculate R_s only of adjacent pairs not of all pairs of peaks; the result is satisfactory if the peaks do not all have the same relative order of retention in the experimental runs. Minimal resolution was selected in every simplex iterative proceeding. The result selects the highest resolution for the worst separated pair of peaks as a criterion of separation. All the other pairs of peaks give larger resolution values.

The SDO-G method can be used to carry out this optimization procedure. The above series of ten compounds were applied for the two-factor (carrier gas flow-rate and column temperature) optimization in GC. Table I gives the experimental k' values and Table II the b. coefficients. The experimental boundary conditions are carrier gas flow-rate = 10–30 ml/min, column temperature = 150–180°C and analysis time

TABLE I

k' VALUES OF TEN COMPOUNDS MEASURED BY GC USING DIFFERENT CARRIER GAS FLOW-RATES AND COLUMN TEMPERATURES

Chromatography[a]			*Compound No.*[b]									
No.	*F (ml/min)*	*T (°C)*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
1	10	150	2.258	2.725	3.358	3.667	4.625	5.358	6.792	8.917	10.790	15.367
2	10	165	1.941	2.291	2.789	2.981	3.663	4.258	5.519	6.681	7.424	10.752
3	10	180	1.725	1.963	2.637	2.486	3.018	3.376	4.009	5.037	5.300	7.743
4	20	150	2.181	2.663	3.265	3.554	4.470	5.229	6.578	8.711	10.520	14.879
5	20	165	1.895	2.263	2.763	2.974	3.645	4.184	5.118	6.592	7.434	10.671
6	20	180	1.662	1.883	2.247	2.389	2.857	3.234	3.818	4.779	5.117	7.415
7	30	150	2.138	2.615	3.185	3.492	4.385	5.108	6.400	8.492	10.260	14.538
8	30	165	1.869	2.180	2.705	2.869	3.541	4.049	4.951	6.377	7.180	10.311
9	30	180	1.672	1.914	2.276	2.396	2.914	3.276	3.914	4.879	5.207	7.586

[a] F = carrier gas flow-rate; T = column temperature.

[b] Compounds: 1 = isoamyl acetate; 2 = dodecane; 3 = chlorobenzene; 4 = 1,3,5-trimethylbenzene; 5 = *o*-chlorotoluene; 6 = bromobenzene; 7 = *m*-dichlorobenzene; 8 = *o*-dichlorobenzene; 9 = diethyl malonate; 10 = 1,4-butyrolactone.

TABLE II

VALUES OF THE COEFFICIENTS b_0, b_1,b_2, b_{11},b_{22} AND b_{12} OF THE TEN COMPOUNDS AND COR RELATION COEFFICIENT, r

Compound No.[a]	b_0	b_1	b_2	b_{11}	b_{22}	b_{12}	r
1	103.287	−82.565	−4.336	16.719	0.198	1.658	0.9994
2	128.070	−102.217	−3.157	20.555	−0.002	1.342	0.9983
3	187.891	−161.529	10.163	35.532	0.749	−5.618	0.9887
4	134.894	−101.818	−4.607	19.108	−0.131	2.107	0.9990
5	244.225	−192.618	−8.125	38.090	0.251	3.238	0.9987
6	243.506	−186.804	−7.952	35.651	−0.048	3.466	0.9993
7	461.392	−368.403	−16.474	73.472	0.047	7.161	0.9991
8	651.345	−525.547	−13.987	106.016	−0.042	6.078	0.9994
9	1437.433	−1210.240	−22.895	254.893	−0.654	10.788	0.9996
10	1863.054	−1557.112	−37.881	325.710	−0.021	16.666	0.9996

[a] See Table I.

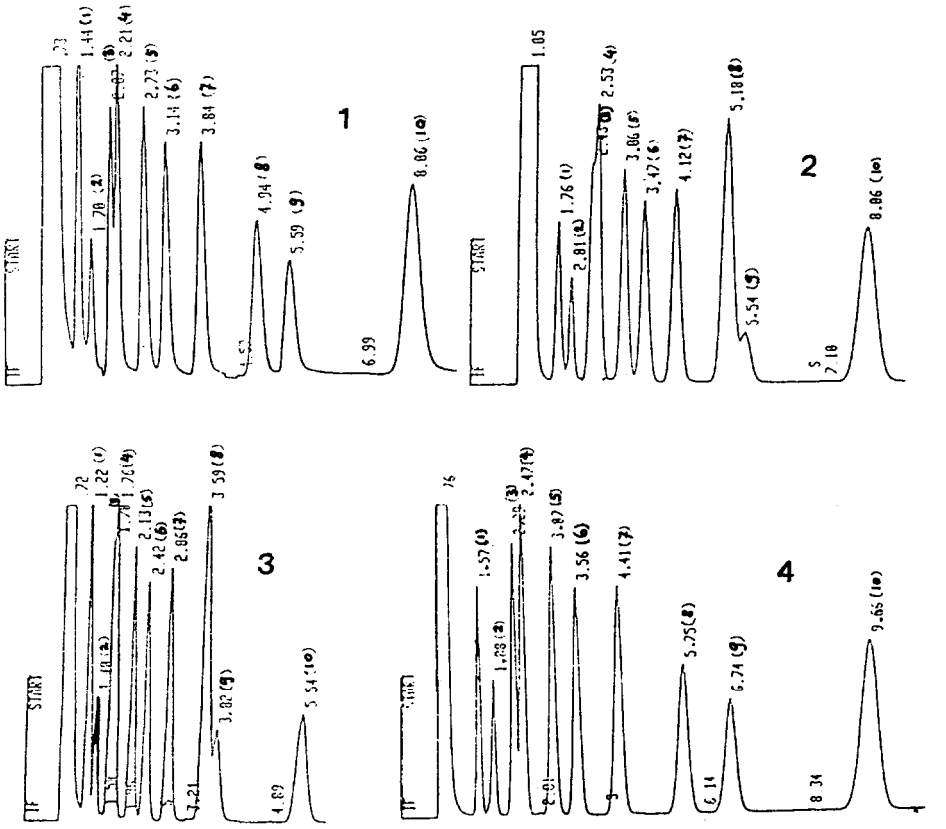

Fig. 2. Experimental chromatograms obtained under the following conditons: (1) T = 165°C, F = 20 ml/min. (2) T = 180°C, F = 10 ml/min. (3) T = 180°C, F = 20 ml/min. (4) T = 157.7°C, F = 19.4 ml/min. Numbers at the peaks indicate retention times in min, and (in parentheses) compound Nos. (as in Table I).

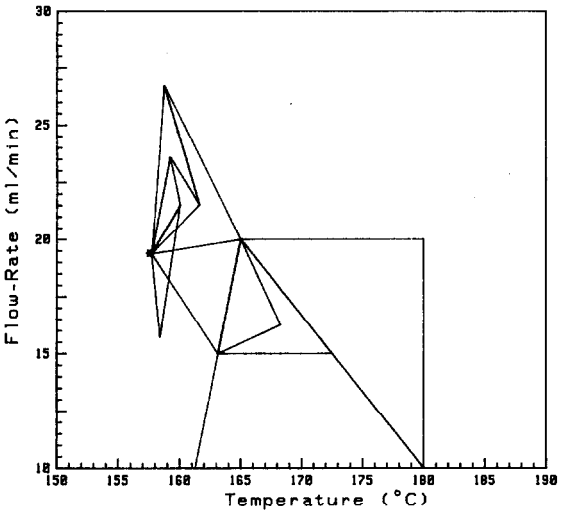

Fig. 3. Simplex optimization using SDO-G.

TABLE III

RESULTS OF THE COMPUTER-ASSISTED SIMPLEX PROCESS

No.	*Temperature (°C)*	*Flow-rate (ml/min)*	*Resolution, R_s*
1	165.00	20.0	0.9809
2	180.00	10.0	0.4601
3	180.00	20.0	0.4181
4	161.25	10.0	0.7195
5	172.50	15.0	0.5395
6	150.00	22.5	0.0000
7	171.56	12.5	0.4068
8	165.00	20.0	0.9809
9	172.50	15.0	0.5395
10	163.13	15.0	0.9418
11	163.13	15.0	0.9418
12	151.41	21.3	0.0000
13	168.28	16.3	0.7889
14	164.06	17.5	0.9750
15	157.73	19.4	1.1454
16	151.41	21.3	0.0000
17	164.06	17.5	0.9750
18	158.73	26.7	1.0399
19	161.37	19.7	1.0702
20	150.00	27.6	0.0000
21	161.62	21.5	1.0636
22	158.23	23.0	1.1049
23	161.09	11.0	0.8171
24	159.20	23.6	1.0855
25	159.68	20.4	1.1051
26	153.75	21.4	0.0000
27	160.04	21.5	1.0931
28	158.47	21.5	1.1192
29	158.42	15.7	1.1105
30	158.89	20.4	1.1197
31	155.13	11.6	0.0000
32	159.06	19.5	1.1196
33	158.08	17.5	1.1378

control $k' = 13$. Three initial experiments were required, which can be selected repeatedly from the nine preliminary experiments to perform the simplex process and obtain the maximum R_s. The initial experimental condition are (1) $T = 165°C$, $F = 20$ ml/min, (2) $T = 180°C$, $F = 10$ ml/min and (3) $T = 180°C$, $F = 20$ ml/min (T = column temperature, F = carrier gas flow-rate).

The chromatograms of three initial experiments are shown in Fig. 2 and results for SDO-G are given in Fig. 3 and Table III. Thirty-three iterative processes were performed by the computer; processes 6, 12, 20, 26 and 31 attempted to cross boundaries and were assigned an R_s of zero. The maximum R_s (1.12) is the highest resolution for the worst separated pair of peaks. The optimum conditions are a carrier gas flow-rate of 19.4 ml/min and a column temperature of 157.7°C. The same result was obtained from the general sequental simplex method. Fig. 2 shows the chromatogram of the ten compounds using these conditions. Excellent agreement was obtained between the predicted and experimental results.

Comparing experiments with the SDO-G method and the general sequential simplex method, ten and about thirty-three experiments (Table III), respectively, were required. In addition, SDO-G can select repeatedly the initial simplex experiments from the nine preliminary experiments without any additional experiment and the result gives the maximum R_s. Therefore the SDO-G method has distinct advantages over the general sequental simplex method for two-factor optimization in GC.

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