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Short Communication

Optimization of separation of rare earths in high-performance thin-layer chromatography

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ABSTRACT

A computer-assisted method is presented for simultaneous two-factor optimization (acidity and extractant concentration) for the optimum separation of ten rare earths (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho and Er) by high-performance thin-layer chroamtography. The method is based on a polynomial estimation from seven preliminary experiments according to a hexagon design. The computer scanning technique was used in two-dimensions. The R_F difference was used as the selection criterion. Good agreement was obtained between predicted data and experimental results.

INTRODUCTION

In recent years, several papers have been published on the advanced separation of rare earths by thin-layer chromatography (TLC) [1–8]. Mostly the mobile phase used was a mixture that included an organic solvent, extractant and acid. Generally, the composition of the mobile was tested empirically for synergistic effects. This was carried out on a trial-and-error basis, which leads to results often not as good as might be expected in an optimum separation. Systematic strategies to optimize mobile phase composition in high-performance TLC (HPTLC) has rapidly gained widespread acceptance. Sequential simplex [9,10] window diagram [11,12], overlapping resolution map [13,14] and statistical scanning techniques [15] have been employed for optimization of HPTLC. Recently we have described a computer-assisted optimization of two-factor selectivity in HPTLC [16].

In general, the mobile phase systems have usually involved an organophosphorus extractant, an oxygen-containing solvent (ether or ketone) and an acid for the separation of rare earths by TLC. This work was undertaken in order to develop a simpler and more convenient system for the separation of rare earths by HPTLC. A computer-assisted optimization method is presented for simultaneous two-factor (acidity and extractant concentration) optimization of the separation of ten rare earths (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho and Er) by HPTLC.

The principle of the method is based on a polynomial between the retardation factor, R_F, and the two factors considered. In order to investigate the effect of two variables in HPTLC and their possible interaction, a Dochlert matrix design (Fig. 1) was adopted as the optimization strategy [17]. Seven preliminary experiments represent the three different levels in which the R_F values were obtained. These values were then substituted into the following equation, in order to establish the values of the constants:

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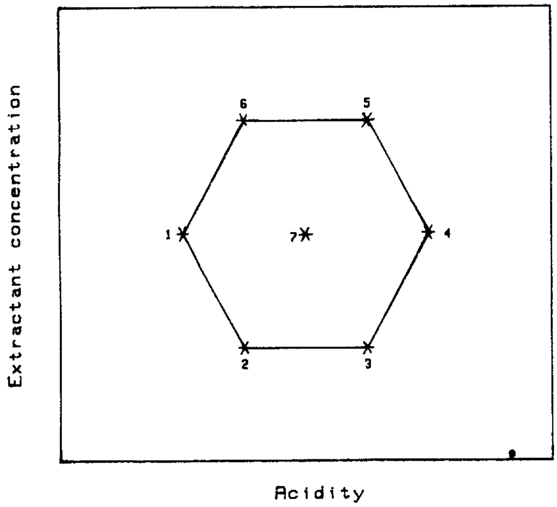

Fig. 1. Hexagon design for two-factor effects.

$$R_F = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad (1)$$

where X_1 and X_2 are the two factors of unrelated variables and b_0, b_1, b_2, b_{11}, b_{22} and b_{12} are constants characteristic of a given compound. According to eqn. 1, the R_F values of the compounds can be predicted at all two-factor compositions within the rectangular region.

The difference between R_F values was used as the separation criterion for indication of chromatographic performance:

$$\Delta R_F = |R_{F(i)} - R_{F(j)}| \quad (2)$$

The method allows the determination of ΔR_F only for adjacent pairs of spots and not for all pairs. If n is the spot number, $n - 1$ spot pairs are calculated in each two-factor composition within the selected rectangle. The predicted R_F values of the solutes are arranged in order before calculating every ΔR_F in all two-factor compositions. The result is satisfactory even if not all the spots have the same relative order of R_F values in the experimental runs.

A ΔR_F contour map was constructed to calculate all adjacent pair ΔR_F values and to select the minimum ΔR_F in every two-factor composition. A maximum ΔR_F was then selected in all two-factor compositions. The maximum ΔR_F was selected for the worst separated spot pair as the separation criterion. All other spot pairs have larger ΔR_F values.

The computer program DOS-T (di-factor optimization system for TLC) was used for the optimization of the separation of a mixture of ten rare earths. Good results were obtained between the predicted data and experimental results.

EXPERIMENTAL

Materials

All chemicals were of analytical-reagent grade. Test solutions of rare earths were prepared by dissolving appropriate amount of the oxides ($>99.9\%$) in 7.2 *M* nitric acid and evaporating to dryness, followed by dissolution in 0.1 *M* nitric acid to give a 5 mg/ml metal solution. Commercially available precoated HPTLC silica plates from Merck (Darmstadt, Germany) were used. All plates were preliminarily developed with the 2.5 *M* ammonium nitrate solution as the mobile phase, then heated at *ca.* 70°C for 1 h before use.

The mobile phase components were mixed in different ratios as given in Table I. The four constituents were (A) 4-methyl-2-pentanone, (B) tetrahydrofuran (THF), (C) nitric acid and (D) the mono-2-ethylhexyl ester of 2-ethylhexylphosphonic acid (P507, No. 1 Chemical Reagent Factory, Tianjin, China).

Apparatus

A CAMAG (Muttenz, Switzerland) Nanomat sampler, linear developing chamber and TLC plate heater II were used.

All computer studies were carried out on a Model HP-220 microcomputer (Hewlett-Packard, Palo Alto, CA, USA) with an HP-9133A disk drive and HP-7470A graphics plotter. The DOS-T program was written in HP BASIC 4.

Chromatography

Volumes of 200 nl of aqueous solutions were spotted by means a Pt–Ir pointed glass capillary. Separation was carried out using linear development with the mobile phases given in Table I. A typical development required the solvent front to move 50 mm from the origin. After development, the HPTLC plate was dried thoroughly by blowing warm air and the positions of the rare earths were revealed by

TABLE I

R_F VALUES OF TEN RARE EARTHS MEASURED BY HPTLC USING DIFFERENT MOBILE PHASE COMPOSITIONS

Mobile phase composition (ml)[a]				R_F[b]									
A	B	C	D	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er
3.00	1.50	0.40	0.42	0.05	0.11	0.15	0.21	0.42	0.49	0.54	0.62	0.69	0.78
3.00	1.50	0.58	0.14	0.02	0.04	0.05	0.07	0.13	0.15	0.15	0.20	0.34	0.39
3.00	1.50	0.94	0.14	0.01	0.01	0.02	0.03	0.06	0.07	0.08	0.11	0.16	0.22
3.00	1.50	1.12	0.42	0.01	0.03	0.04	0.06	0.11	0.14	0.17	0.26	0.35	0.43
3.00	1.50	0.94	0.70	0.02	0.06	0.08	0.09	0.23	0.29	0.31	0.45	0.64	0.73
3.00	1.50	0.58	0.70	0.06	0.14	0.21	0.27	0.54	0.63	0.69	1.0	1.0	1.0
3.00	1.50	0.76	0.42	0.02	0.04	0.07	0.08	0.18	0.20	0.25	0.35	0.44	0.46

[a] For designation of A, B, C and D, see the text.

[b] R_F values are the mean of four measurements; the relative standard deviation is less than 6% on different plates.

spraying with saturated alizarin–ethanol solution and then treatment with ammonia vapour, followed by gentle heating. The rare earths were all detected as violet spots on a pale yellow background.

RESULTS AND DISCUSSION

A series of ten rare earths were applied for two-factor (volume of HNO_3 and P507) optimization. The measured R_F values used in the optimization are listed in Table I and the coefficients *b* in Table II.

In Table I the R_F values of the rare earths increase with increasing concentration of P507 and decrease with increasing concentration of HNO_3. The effects of P507 and HNO_3 on R_F are complicated, so the selction of the optimum composition of P507 and HNO_3 is difficult. DOS-T can be selct the composition of P507 and HNO_3 with only seven preliminary experiments.

Figs. 2 and 3 show the DOS-T ΔR_F contour maps (stereo and planar). Note that in Fig. 3 the white region is designated as the optimum two-factor composition, where the value of ΔR_F between all possible spot pairs is equal to or better than the desired value ($\Delta R_F = 0.04$). The point of the maximum ΔR_F value (0.05) is marked by with a cross; here the optimum condition of the two-factor composition is 0.46 ml each of HNO_3 and P507. In practice the composition 4-methyl-2-pentanone–

TABLE II

VALUES OF COEFFICIENTS $b_0, b_1, b_2, b_{11}, b_{22}$ AND b_{12} FOR TEN RARE EARTHS AND CORRELATION COEFFICIENT (*r*), *F*-TEST (*F*) AND STANDARD DEVIATION (*s*)

Rare earth	b_0	b_1	b_2	b_{11}	b_{22}	b_{12}	*r*	*F*	*s*
La	0.0553	−0.1150	0.1042	0.0772	0.0638	−0.1488	0.9964	83.727	0.0024
Ce	0.1670	−0.3727	0.1617	0.2315	0.1913	−0.2480	0.9943	51.741	0.0071
Pr	0.1052	−0.2608	0.4261	0.1929	0.1754	−0.4960	0.9924	38.980	0.0118
Nd	0.2367	−0.5941	0.5322	0.4244	0.2710	−0.6944	0.9913	34.057	0.0165
Sm	0.4004	−0.9599	1.0074	0.6559	0.4943	−1.1905	0.9978	137.147	0.0165
Eu	0.5590	−1.3256	1.0025	0.8873	0.7175	−1.2897	0.9984	185.783	0.0165
Gd	0.4274	−1.1366	1.5213	0.8102	0.3986	−1.5377	0.9982	167.554	0.0188
Tb	0.2257	−0.7269	2.0288	0.6944	0.8610	−2.2818	0.9881	24.744	0.0660
Ho	0.6820	−1.1281	0.8928	0.6173	0.9566	−0.8929	0.9929	41.785	0.0471
Er	1.1287	−2.0201	0.4261	1.1188	1.1320	−0.4960	0.9985	195.464	0.0212

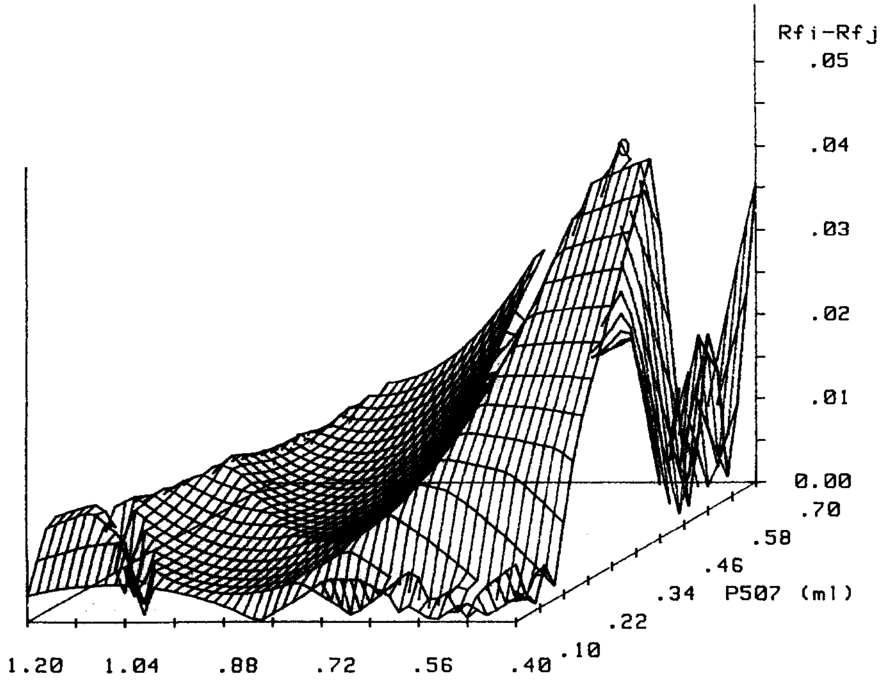

Fig. 2. ΔR_F stereo resolution map for ten rare earths in HPTLC.

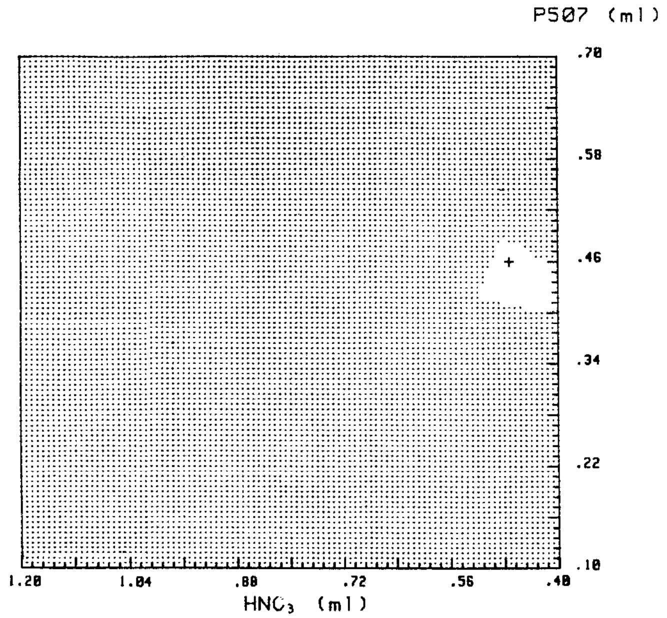

Fig. 3. ΔR_F planar map for ten rare earths in HPTLC.

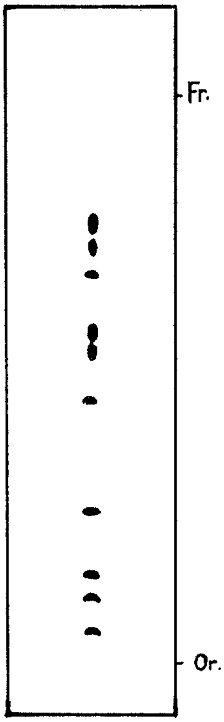

Fig. 4. Chromatogram of the ten rare earths using the optimum mobile phase composition: 4-methyl-2-pentanone–THF–HNO_3–P507 (3.00:1.50:0.46:0.46).

TABLE III

COMPARISON OF PREDICTED AND OBSERVED R_F VALUES FOR TEN RARE EARTHS UNDER OPTIMUM CONDITIONS

R_F	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er
Predicted	0.05	0.11	0.15	0.21	0.41	0.48	0.54	0.67	0.72	0.77
Observed[a]	0.06	0.12	0.16	0.27	0.47	0.55	0.59	0.69	0.74	0.78

[a] R_F values are the means of four measurements, the relative standard deviation is less than 5% on different plates.

THF–HNO_3–P507 = 3.00:1.50:0.46:0.46 (v/v/) was used for separation and the results are shown in Fig. 4. Table III gives the experimental and predicted results using this optimum condition composition; they are in good agreement.

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