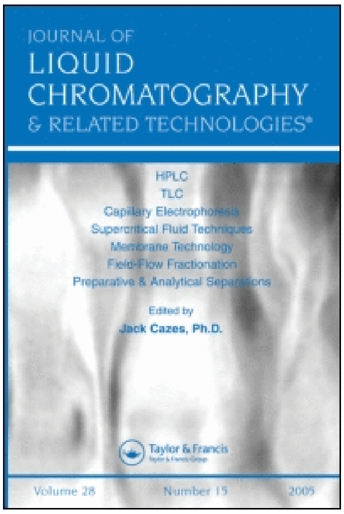

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W. Markowski[a]; K. L. Czaplnska[a]; M. Blaszczak[b]
[a] Department of Inorganic and Analytical Chemistry, Medical Academy, Staszica, Poland [b] Department of Mathematics, Medical Academy, Al. Raclawickie, Poland

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DETERMINATION OF THE CONSTANTS OF THE SNYDER-SOCZEWINSKI EQUATION BY MEANS OF GRADIENT MULTIPLE DEVELOPMENT

W. MARKOWSKI[1], K. L. CZAPINSKA[1],
M. BLASZCZAK[2]
[1]*Department of Inorganic and Analytical Chemistry*
Medical Academy
20-081 Lublin
Staszica 6, Poland
[2]*Department of Mathematics*
Medical Academy
20-059 Lublin
Al. Raclawickie 1, Poland

ABSTRACT

Two - parameter equation which follows from the Snyder - Soczewinski competitive adsorption model describes the retention - eluent composition relationships for numerous solutes both in normal phase as well as reversed-phase systems. Its parameters for a given system can be determined from series of isocratic experiments or by reversed gradient multiple development.

In the present paper a two-step gradient development was applied. A method of solution of sets of equations leading to calculation of parameters k_0 and m of the equation:

$$\log k = \log k_0 - m \log c$$

is reported.

INTRODUCTION

In recent years an increasing popularity of high performance thin-layer chromatography has been observed; this is due to low cost, simplicity, short time of analysis, possibility of parallel analysis of numerous samples. Modern densitometers transformed HPTLC in an accurate method of microanalysis; the same chromatogram can be scanned at several wavelengths which facilitates at different wavelengths. A new dimension is the combination of HPTLC with other chromatographic methods to increase the effectiveness of separation.

The optimization of the separation process is important especially in the case of complex samples and can be carried out by many methods [1-3]. One of the elements of the integral process of optimization is the choice of the eluent and its composition. In most methods multicomponent eluents are used. To choose the optimal composition of a multicomponent system the knowledge of the behaviour of the solutes in simpler - binary solvent systems is required [4]. From the characteristics of solute retention in binary systems the optimal composition of eluent in ternary system can be found, e.g., by the PRISMA model [5]. The behaviour of solutes in a binary solvent system may frequently be described by a two-parameter equation [6,7]. The constants of this equation are usually determined from log k′ vs. c plots for a series of isocratic experiments (c - concentration of modifier in mole or volume fraction). For multicomponent samples of wide range of polarities of the components a more promissing technique is gradient elution which also requires the knowledge of retention vs. composition relationships. In the present paper we describe an attempt to apply the principle of reverse gradient in version of two-step development to characterize the components of multicomponent samples and to determine the retention-eluent composition relationships. These relationships can then be used for further optimization of the separation depending on the purpose of analysis and criteria assumed.

THEORETICAL CONSIDERATIONS

The process of multiple development with increasing development distances and reverse gradient (decreasing elution strength for consecutive developments, evaporations of solvent after each step) has been discussed in detail in earlier papers [8,9]. The final R_F value for the simplest case of reverse - gradient double development and increasing development distance can be calculated from the following equation [8]:

$$R_{FGh(j)} = z_{(1)} R_{F(1,j)} + [1 - R_{F(1,j)} z_{(1)}] R_{F(2,j)} \quad (1)$$

Let us assume that two experiments are carried out. In the first the development distance was $z_{(1)}$ with an eluent of concentration of the modifier $c_{(1)}$; then the plate is dried. In the second stage the distance was $z_{(2)}=1.0$, with an eluent of $c_{(2)} < c_{(1)}$. In the second experiment the first development distance is $z_{(3)}$ with an eluent of concentration $c_{(3)}$, the plate is dried as in the first experiment and then developed with eluent of concentration $c_{(4)}$ to distance of $z_{(4)}=1.0$. In both experiments the same plates are used and eluents $c_{(1)}$ - $c_{(4)}$ have the same qualitative composition and differ only in the concentrations of the modifier. We have thus two equations for the final R_F of the solute j:

$$R_{FG1(j)} = z_{(1)} R_{F(1,j)} + [1 - R_{F(1,j)} z_{(1)}] R_{F(2,j)} \quad (2)$$

$$R_{FG2(j)} = z_{(3)} R_{F(3,j)} + [1 - R_{F(3,j)} z_{(3)}] R_{F(4,j)} \quad (3)$$

The R_F values of individual solutes j can be expressed by their characteristic parameters. If the relationships are given by two - parameters equation which follows the Snyder-Soczewinski model [6,7]:

$$\log k_{(i,j)} = \log_{o(j)} - m_{(j)} \log c_{(i)} \quad (4)$$

then the R_F value is equal to:

$$R_{F(i,j)} = \frac{1}{1 + \frac{k_{o(j)}}{c_{(i)}^{m(j)}}} \quad (5)$$

If eq.(5) is substituded to eqs., (2,3) then after transformation we have the following set of equations:

$$R_{FG1(j)} k_{o(j)}^{2} + k_{o(j)} [R_{FG1(j)} c_{(2)}^{m(j)} + R_{FG1(j)} c_{(1)}^{m(j)} - z_{(1)} c_{(1)}^{m(j)}] - [R_{FG1(j)} - 1] c_{(1)}^{m(j)} c_{(2)}^{m(j)} \quad (6)$$

$$R_{FG2(j)} k_{o(j)}^{2} + k_{o(j)} [R_{FG2(j)} c_{(4)}^{m(j)} + R_{FG2(j)} c_{(3)}^{m(j)} - z_{(3)} c_{(3)}^{m(j)}] - [R_{FG2(j)} - 1] c_{(3)}^{m(j)} c_{(4)}^{m(j)} \quad (7)$$

in which k_o and m are unknown. The remainning values are known and the values of $R_{FG1(j)}$ and $R_{FG2(j)}$ are determined experimentally in two experiments as described above. The set of eq., (6,7) can be solved by approximation methods; no analytical solution exists. The following procedure is applied. Eqs., (6,7) are quadratic with respect to k_o. Therefore, we determine for eq., (6) for which values of m the equation is sensible, i.e $\Delta \geq 0$. Then its solution are given by equations:

$$k_o^{(1)} = \frac{(-b+\sqrt{\Delta})}{2a} \tag{8a}$$

$$k_o^{(2)} = \frac{(-b-\sqrt{\Delta})}{2a} \tag{8b}$$

Since the root given by eq.(8b) is always negative, it is discarded. The root calculated from eq. (8a) for a given m values is calculated assuming that $\Delta \geq 0$. The root is introduced to eq.(7) and the polynom obtained is checked:

$$F(m) = R_{FG2(j)} k_{o(j)}^2 + k_{o(j)} [R_{FG2(j)} c_{(4)}^{m(j)} + R_{FG2(j)} c_{(3)}^{m(j)} - z_{(3)} c_{(3)}^{m(j)}] - [R_{FG2(j)} - 1] c_{(3)}^{m(j)} c_{(4)}^{m(j)} \tag{9}$$

The polynom F·is checked relative to the change of sign: if for a certain value of m1, F_1>=0, and for another m2 >m1, F_2<=0 or if the opposite is true, that is, F_1<=0 and F_2>=0, then the polynom can be solved, e.g., by the bisection method [10]. Defining the accuracy of solution of the polynom (ϵ),we find the value of m, and then from eq. (6) or (8) the corresponding value k_o,thus obtaining the two necessary parameters of eqs. (5) and (9). The procedure was applied to elaborate a computer program. The starting data for a given solute are the values of R_{FG1} and R_{FG2} obtained in two different gradient experiments and development distances $z_{(1)}$ and z(3), modifier concentration $c_{(1)}$ and $c_{(4)}$ in the individual stages of development and the epsilon value, i.e., the accuracy with which the zero value of polynom is determined. If there is no solution, an appropiate answer is given. The program has been written in Pascal (version 6.0).

EXPERIMENTAL

The chromatografic experiments were carried out using a horizontal sandwich chamber DS (Chromdes, Lublin, Poland) [11,12]. Precoated 10 x 5 cm plates covered with 0.25 mm layer of silica Si 60 (E. Merck, Darmstadt, FRG) were used. As model solutes, lipophilic mixture of test dyes (E. Merck), azobenzene and 2-nitroaniline were used, chromatographed in the system heptane - diisopropyl ether. The total development distance was 80 mm.

RESULTS AND DISCUSSION

As stated in the Introduction, the relationship between retention and eluent composition is frequently represented by a straight line in the system of cordinates log k′ vs. log c. The equation (4) is characterized by two parameters: the slope m and the value k_0 (k′ for pure modifier, c=1). It follows from numerous experimental results [4] that the equation is approximate and that deviations from linear relationships are observed especially for low and high concentration of modifier. The log k′ vs. log c plots for a whole group of substances investigated permits the estimation of selectivity and range of k′ values which allows for the choice of suitable modifier concentration for a given set of solutes; this constitutes the basis of the optimization process.

The solutes were chromatographed in isocratic runs for several concentrations of diisopropyl ether in heptane. From the R_M (log k′) vs. log c plots the k_0 and m vaues were determined by the least squares method (Table 1).

Since reverse - gradient two - stage development was used, the final R_{FG} values were calculated (Table 3) using an equation and computer program derived earlier [8] for the gradient programs applied (Table 2 - development distances and modifier concentrations).

Table 1

The comparison of coefficients k_0 and m calculated from isocratic measurement of R_F (in the range of modifier from 0.2 to 0.4 volume fraction) and calculated from gradient data.

CODE	Isocratic mode			Gradient mode	
	k_0	m	r	k_0	m
Azobenzene 1	0.139	0.99	0.9981	0.116	1.25
Azobenzene 2	0.241	1.44	0.9409	0.208	1.55
4-Dimethylamino-azobenzene	0.336	1.15	0.9555	0.192	1.58
Indophenole Blue	0.447	1.82	0.9424	0.214	2.33
Sudan Red G	0.751	1.51	0.9672	0.286	2.22
Orto-nitroaniline	0.698	1.49	0.9407	0.203	2.55
Meta-nitroaniline	1.309	1.52	0.7824	0.639	2.25
Para-nitroaniline	2.53	1.66	0.9603	3.52	1.75

Two gradient experiments permitted to obtained pairs of R_{FG1} and R_{FG2} values for each solute (Table 3).

Applying the method of solution of the pair of equations described above and the computer program (Fig.1) the constants k_0 and m for each solute were calculated (Table 1). The values thus obtained can be used to determine log k′ vs. log c lines and to charactrize the system (sample, eluent, adsorbent).

Table 2.

The gradient program used in two - stage development.

RUN	STEP	DISTANCE	CONCENTRATION
#1	1	0.25	0.40
	2	1.00	0.20
#2	1	0.50	0.40
	2	1.00	0.30

Table 3

The comparison of the final values of R_{FG} obtained by simulation of two stage development and in experiments.

CODE	$R_{FG(calc.)}$		$R_{FG(exp.)}$	
	Run #1	Run #2	Run #1	Run #2
Azobenzene 1	0.63	0.77	0.62	0.78
Azobenzene 2	0.34	0.54	0.38	0.58
4-Dimethylamino-azobenzene	0.36	0.54	0.39	0.56
Indophenole Blue	0.14	0.29	0.18	0.36
Sudan Red G	0.13	0.26	0.16	0.32
Orto-nitroaniline	0.14	0.27	0.15	0.32
Meta-nitroaniline	0.08	0.16	0.08	0.17
Para-nitroaniline	0.04	0.08	0.03	0.06

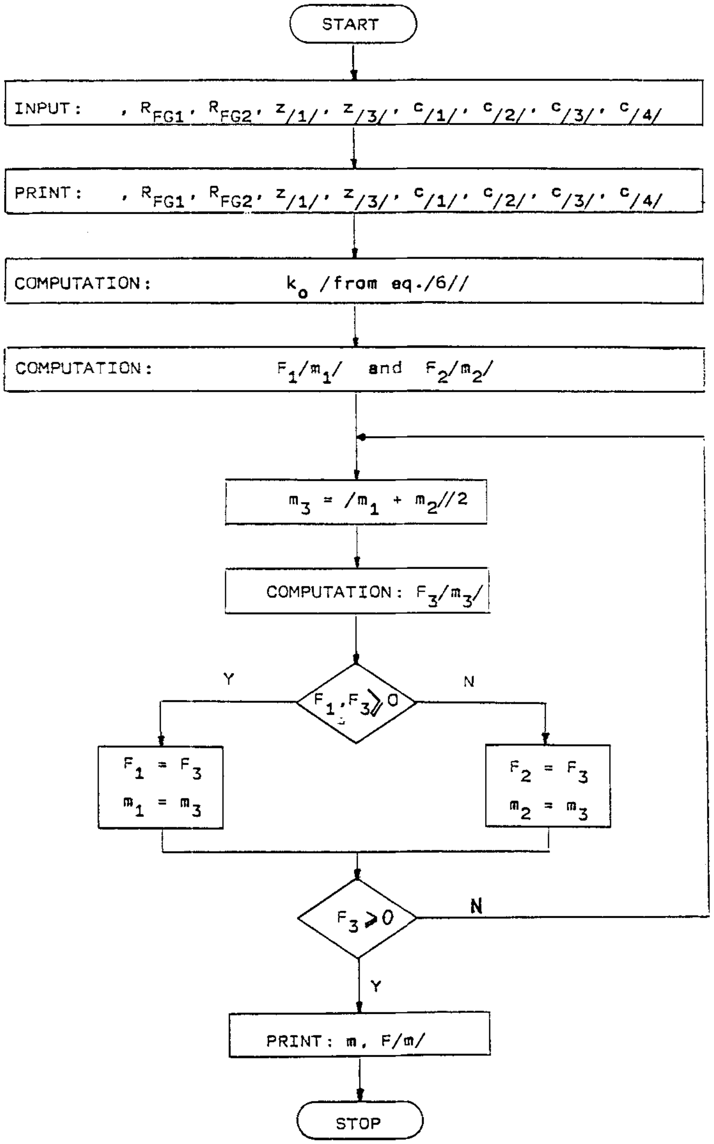

Fig.1 The flow diagram of the computer program for calculation ko and m values

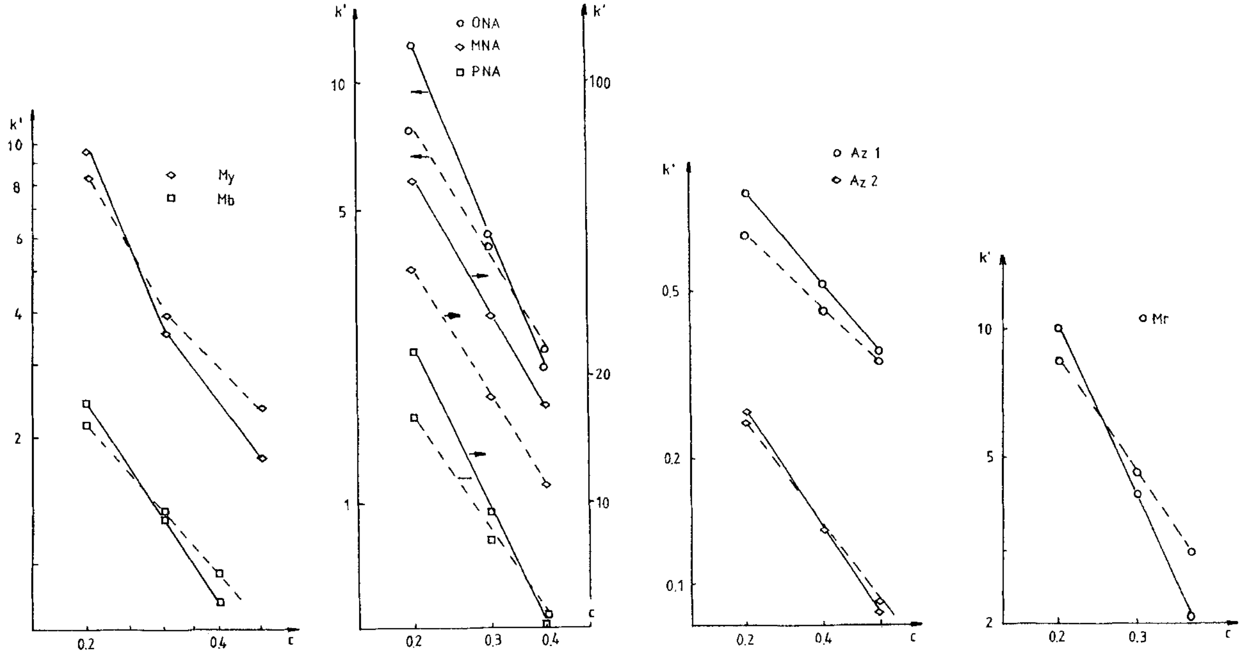

Fig.2 The comparison of log-log plots determined by the isocratic method (the dashed line) and by the two-step gradient (the continuous line) for investigated solutes: Mr - Sudan Red G, Mb - Indophenol blue, My - 4-Dimethylaminoazobenzen, Az1 - Azobenzene 1, Az2 - Azobenzene 2, ONA Orto-nitroanilina, PNA Para-nitroanilina, MNA Meta-nitroanilina

The comparison of the retention - eluent composition relationships obtained by isocratic and stepwise gradient methods is presented in Fig.2. It can be seen from Fig.2 and comparison of the Table 3 and Table 1, that the data from gradient experiment indicated somewhat higher values of slopes m that those obtained from isocratic experiments. Except for 4 - nitroaniline the remaining straight lines are close to each other; sometimes they cross. Taking into account the differences in experimental techniques (isocratic and gradient multiple development) the similarity of results obtained can be considered satisfactory.

The retention - eluent composition relationships can be used for futher optimization procedure.

References

1. S. Habibi-Goudarzi, K.J. Ruterbories, J.E. Steinbrunner and D. Nurok, Computer-Aided Survey of Systems for Separating Steorides: J. of Planar Chromatogr., 1 , (1988), 162

2. G. Matysik, W. Markowski, E. Soczewinski and B. Polak: Computer-Aided Optimization of Stepwise Dradient Profiles in Thin-Layer Chromatography, Chromatographia, 34, No. 5-8, (1992), 302

3. Q.-S. Wang and H.-Y. Wang: Computer-Assisted Comprehensive Optimization of Mobile Phase Selectivity in HPTLC, J. of Planar Chromatogr., 3, (1990), 15

4. W. Markowski: Computer-Assisted Selection of the Optimum Gradient in Thin-Layer Chromatography, J. of Chromatogr., 485, (1989), 517

5. S. Nyiredy, K. Dallenbach-Talke and A. Sticher: The "Prizma" Optimization System in Planar Chromatography, J. of Planar Chromatogr., 1, (1988), 336

6. E. Soczewinski: Solvent Composition Effects in Thin-layer Chromatography System of the Silica Gel-electron donor solvent, Anal. Chem., 41, (1969), 179

7. E. Soczewinski: Coadsorption Effects in Liquid-Solid Systems of the Type Silica-Heptane + Dioxane. I Theoretical Considerations, J. of Chromatogr., 388, (1987), 97

8. W. Markowski and E. Soczewinski: Computer-aided Optimization of Gradient Multiple-development Thin-layer Chromatography, I Two-stage Development, J. of Chromatogr., 623, (1992), 139,

9. W. Markowski: Computer-aided Optimization of Gradient Multiple-development Thin-layer Chromatography, II Multi-stage Development, J. of Chromatogr., accepted for publication

10. E. Slavicek: Computing Techniques for Chemists, (in polish), WNT, Warsaw 1991

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