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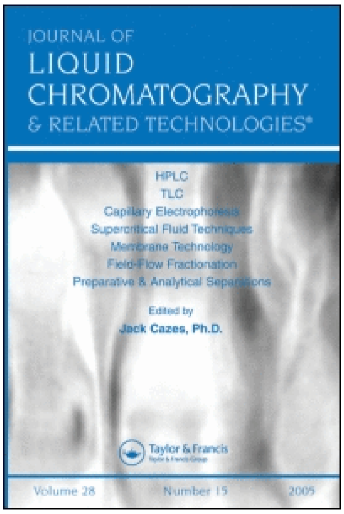

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SELECTION OF CRITERIA FOR COMPARING AND EVALUATING THE OPTIMIZATION OF SEPARATION IN ION CHROMATOGRAPHY

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ABSTRACT

Optimization procedures in Ion Chromatography require unambiguous goals. Optimization criteria express such goals in mathematical terms. If the retention factor t_R, varies as a function of the parameters to be optimized, criteria should be selected that enable simultaneous optimization of retention and selectivity. The non – suppressed Ion Chromatographic method with conductometric detection is described for simultaneous determination of six inorganic anions: fluoride, chloride, nitrite, bromide, nitrate, and sulphate. It is demonstrated that the result of the optimization process depends on the optimization criterion selected. The computer-simulated chromatograms were used for the comparison of optima calculated using four different criteria. General recommendations for double criteria optimization of separation in ion chromatography are suggested.

INTRODUCTION

Ion Chromatography has advanced rapidly owing to its numerous advantages: separation before detection, increased detection, increased sensitivity, simple sample preparation, and faster analysis time.[1]

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Computer optimization procedures, using computer programs to select chromatographic conditions leading to the achievement of a desired separation, have found extensive application in liquid chromatography.[2] Each of the optimization methods has advantages and disadvantages, and none address all users needs. In the past, hidden difficulties in the practical application of computer - assisted method development have discouraged its widespread use. By using the different optimization methods in an integrated manner, it is, however, possible both to speed method development, by reducing unnecessary experimentation, and to overcome many shortcomings of each method, because of the different approaches.

Most computer assisted optimization procedures are based on retention modeling.[3,4] The retention model that describes the relationship between retention time (t_R or capacity) and investigated parameter allows retention times to be predicted for any set of parameters in a search area.[5,6,7] The readability of these predicted retention times is dependent on suitability of the retention model used. However, it is very important to use a proper objective function for evaluating and optimising of a separation. This objective function in ion chromatography must be an optimisation criterion that faithfully reflects the quality of the chromatogram. Because it is difficult to determine unequivocally some single physical value that satisfies the all the requirements of optimization criteria, complex artificial criteria are usually used for this purpose.

This paper compares four criteria which has been suggested in the literature, and suggested a double criteria simulation system for optimization of separation in ion chromatography.

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EXPERIMENTAL

Instrumentation

Samples were analysed using a Metrohm 690 Ion Chromatograph with conductivity detector, and 100 μL injection loop, with Metrohm 687 IC Pump. The separation column, Metrohm IC Anion Column Super Sep 100 x 4.6 mm, was packed with polymethacrylate with quartenary ammmonium groups, and was used with Metrohm IC Predcolumn cartridge PRP-1. Data acquisition was performed using a Shimadzu integrator model C-R5A Chromatopac. The optimisation and mathematical evaluation of experimental data was achieved by IBM compatible PC using MathCad Professional 7.0 and Mathematica 3.0 software.

Reagents

Stock standard solutions of fluoride, chloride, nitrite, bromide, nitrate, and sulphate were prepared by dissolving appropriate amounts of analytical reagent grade sodium of potassium salts in high purity water. These solutions were diluted to give the multi - anion solutions required.

The mobile phase was 2.5 mmol phtalic acid dissolved in high purity water, followed by pH adjustments with 2-amino-2-hidroxymethyl-1,3-propendiol (pH=4.2), and mixed with acetonitrile (2.5 – 10%).

Analytical reagent grade compounds provided by Fluka was used to prepare the eluent system examined in the present study.

RESULTS AND DISCUSSION

Relations Between the Ion - Chromatographic Parameters

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The mathematical form of the functions, f, relating the chromatographic parameter of retention time, y, to the chromatographic parameter of concentration of acetonitrile in eluent, x_n, is unknown:

$$Y = f(x_n)$$

In order to describe that function in the region where the optimum is to be found, the function was approximated by a generalised polynomial equation of the second order. When the chromatographic parameter of retention time is expressed as a function of independent variable, the polynomial equations can be described by a quadratic equation:

$$Y = a_0 + a_1x + a_2x^2$$

where x represents chromatographic parameter of concentration of acetonitrile in eluent, and y represents observed retention time. The coefficients a_0, a_1, a_2 are constants and they are characteristic of each investigated parameter. The fitting was performed in six experimental points. Figure 1 presents experimental data for optimisation of ion – chromatographic parameters.

The Estimation of the Coefficients of the Polynomial Equation

The optimization procedures deal with the estimation of the coefficients in the polynomial equation in order to describe, as well as possible, the responses of the chromatographic experiment. By using the information contained in the optimized equation, the analyst can alter the dependent variables in the desired fashion and calculate, wherever he wants, respecting the boundaries of response value.

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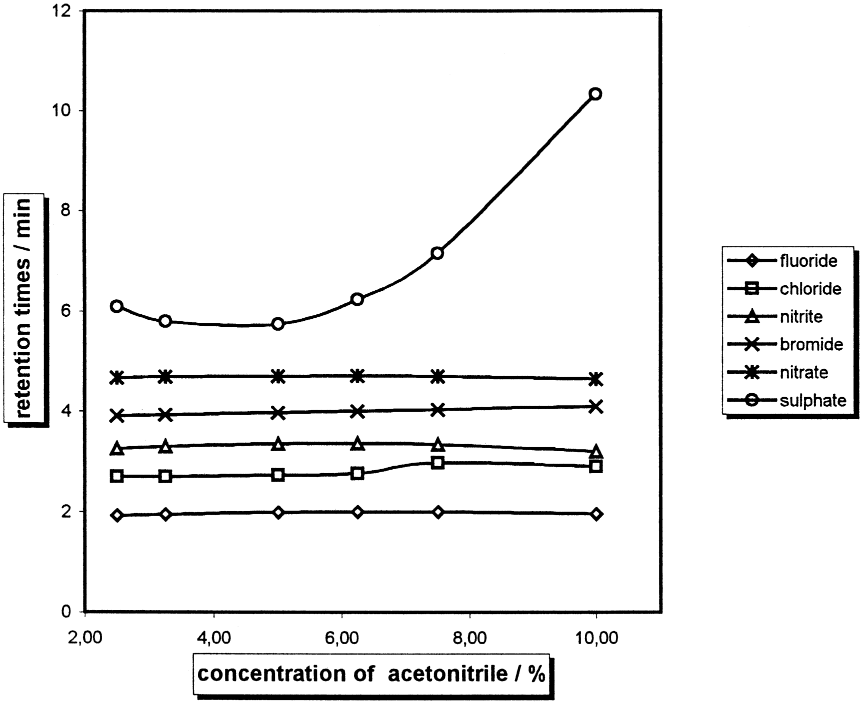

Figure 1. Experimental data of ion chromatographic parameters: plot of retention time t_R against concentration of acetonitrile in eluent.

The coefficients of the polynomial equations must be estimated using statistical methods before the optimal conditions can be calculated in the global optimization process. Since the accuracy of chromatographic response prediction using this model is highly dependent on quality of the estimation of the coefficient, it is, thus, highly dependent on the algorithms and computing program chosen. The coefficients have been estimated (Table 1) employing the polynomial regression model, using MathCad Professional 7.0 and Mathematica 3.0 software.

Criteria for Comparing and Evaluating of Chromatographic Separation

Several criteria for comparing and evaluating of a chromatograph have been suggested in literature and these are summarized below:[7,9,10]

Table 1

Predicted Function with Estimated Coefficients and Correlation Factors for Correlation Between Ion -Chromatographic Parameters of Concentration of Acetonitrile in Eluent and Retention Times

Anion	Response Function	Correlation Factors
Fluoride	$f(x) = -0.0044x^2 + 0.0595x + 1.8012$	0.989
Chloride	$f(x) = 0.003x^2 - 0.0094x + 2.6993$	0.991
Nitrite	$f(x) = -0.0095x^2 + 0.1108x + 3.0382$	0.995
Bromide	$f(x) = 0.0003x^2 + 0.0219x + 3.8503$	0.994
Nitrate	$f(x) = -0.0032x^2 + 0.037x + 4.5989$	0.985
Sulphate	$f(x) = 0.1406x^2 - 1.1905x + 8.1724$	0.989

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Minimum t_R difference, expressed as:

$$\Delta t_{R(min)} = | t_{RFi} - t_{RFj} |$$

t_R values predicted for chromatographic parameters are used to calculate the values of Δt_R for adjacent pairs of chromatographic peaks. If n is the number of peaks, (n-1) calculations are performed for each set of chromatographic conditions. The conditions which give maximum value of $\Delta t_{R(min)}$ present the best separation conditions. If there is a more then one maximum, $\Delta t_{R(min)}$ which has the smallest value, has to be selected. The disadvantage of this method is that it considers only the least well separated pair of peaks.

The Δt_R product is defined as:

$$t^* = \prod_{i=1}^{n} \Delta t_{RFi}$$

where the Δt_R is the difference between a peak and its neighbor. Obviously, because this criterion takes all pairs of peaks into account, it partially overcomes the disadvantage of $\Delta t_{R(min)}$. This criterion depends on the even distribution of all peaks over the chromatogram, and its means, to give highest response when the spots in the chromatogram are as evenly spaced as possible. An obvious disadvantage of these criteria is the loss of individual peak information.

The separation factor, which has been often used for simplex optimisation, can be expressed as:

$$S=\frac{\prod_{i=1}^{n}\Delta t_{RFi}}{t_{RFn}-t_{RF1}}$$

where t_{RFn} is the t_R of peak appearing in the n^{th} place from the point of application of analyte. Note that the numerator is four times the t_{RF} product and the denominator is the distance between the highest and the lowest peaks. Obviously the result obtained from this criterion is similar to that obtained from the Δt_R product.

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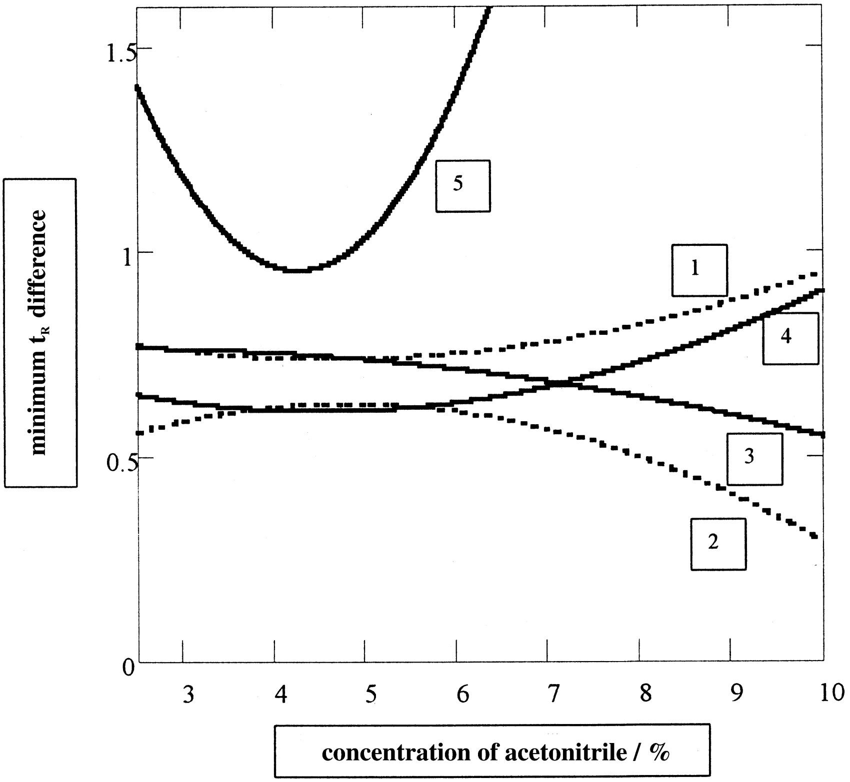

Figure 2. Ion chromatography response surface as a function of concentration of acetonitrile in eluent for minimum t_R difference criteria: 1, fluoride-chloride; 2, chloride-nitrite; 3, nitrite-bromide; 4, bromide-nitrate; 5, nitrate-sulphate.

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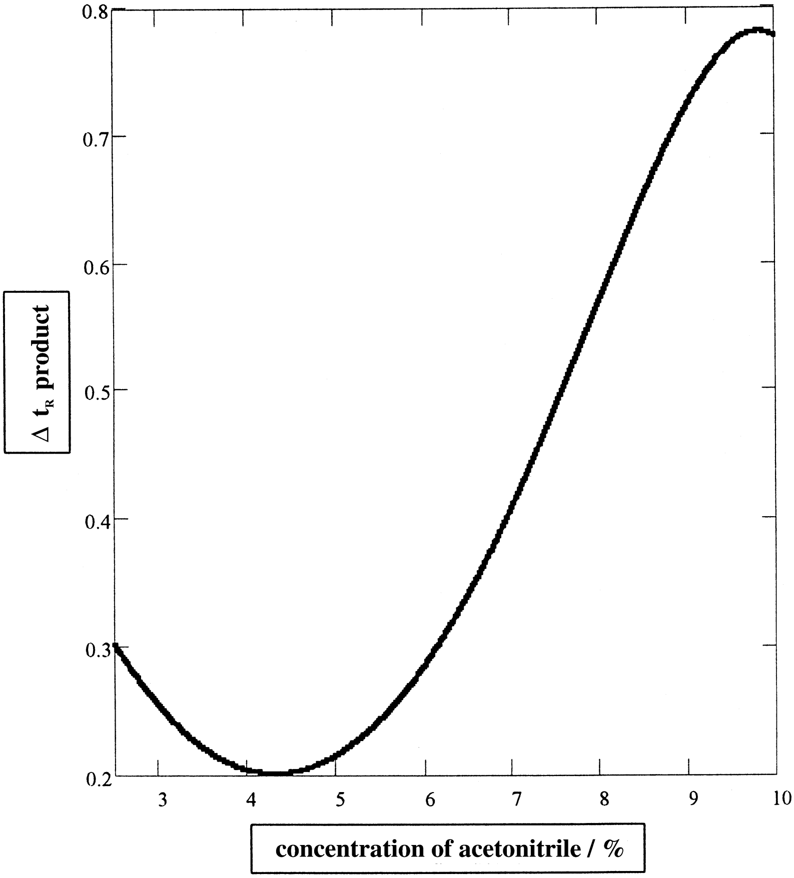

Figure 3. Ion chromatography response surface as a function of concentration of acetonitrile in eluent for Δt_R product criteria.

Multipeak separation response function, MRF is given by the expression:

$$MRF = \frac{\left[\left(ht_{RF\max} - ht_{RFn}\right)\left(ht_{RF1} - ht_{RF\min}\right)\right]}{\left[\left(ht_{RF\max} - ht_{RF\min}\right)/\left(n+1\right)\right]^{n+1}} \prod_{i=1}^{n-1}\left(ht_{RF(i+1)} - ht_{RFi}\right)100$$

where ht_R is defined as t_R x 100. Index 1 corresponds to the component of lowest t_R and index n to that of highest t_R. The boundaries of extreme values, within which all the other components must lie ($t_{R\min}$ and $t_{R\max}$), can be selected to eliminate the regions near the origin and the solvent peak, which are subject

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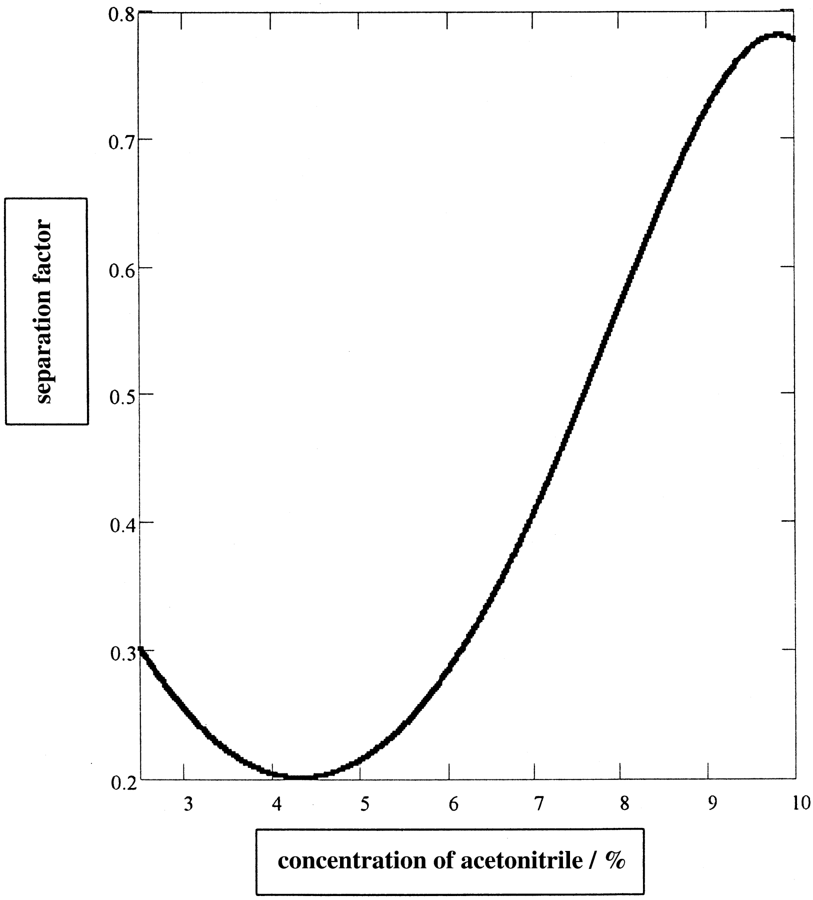

Figure 4. Ion chromatography response surface as a function of concentration of acetonitrile in eluent for separation factor criteria.

to greater qualitative and quantitative uncertainty. The criterion is expressed as a percentage. If a peak does not occur within the present interval then the criterion is automatically set to zero. When all components are equally spaced from each other and form the chosen boundaries the function has its maximum value of 100%.

The four criteria were used for optimization, and behaviour of the four criteria demonstrated for a separation problem. The response surface of four criteria is shown in Figures 2, 3, 4, and 5.

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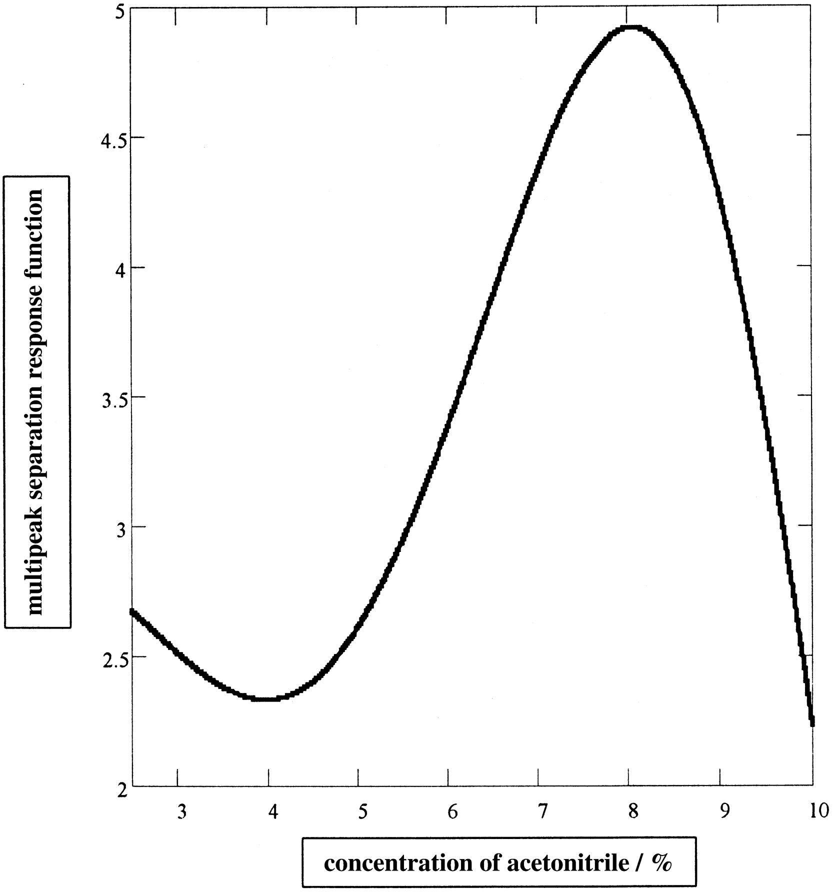

Figure 5. Ion chromatography response surface as a function of concentration of acetonitrile in eluent for multipeak separation response function criteria.

Figure 2 shows that the predicted optima for separation of chloride and nitrate using criteria minimal t_R difference, is at 4.808% acetonitrile in eluent. However, optima for separation of fluoride and chloride, nitrite and bromide, nitrate and bromide lies between 4 and 5%, while separation between bromide and nitrate continuously decrease with increase of acetonitrile. Those results can be used in real sample analysis in following way:

if there is a need for better separation between chloride and nitrite, optima concentration of acetonitrile in eluent is 4.808%

Table 2

Computer Simulated Chromatographic Run in Optimum Conditions Provided by Using Δt_R Product, Separation Factor, and Multipeak Separation Response Function Criteria

Criteria	T	S	MRF
Optimal concentration of Acetonitrile/%	9.824	8.835	8.055
Retention time of fluoride/min	1.961	1.983	1.995
Retention time of chloride/min	2.896	2.850	2.818
Retention time of nitrite/min	3.210	3.276	3.314
Retention time of bromide/min	4.094	4.067	4.046
Retention time of nitrate/min	4.654	4.676	4.689
Retention time of sulphate/min	10.046	8.629	7.705

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if there is a need for better separation between fluoride and chloride, nitrite and bromide, area of optima concentration of acetonitrile in eluent lies in higher values (separation increases within the increase of concentration of acetonitrile)

if there is a need for better separation between nitrate and sulphate, separation continuously increases within increase of concentration of acetonitrile above 5% and within continually decreasing of concentration of acetonitrile below 4%.

Criteria Δt_R product, separation factor, and multipeak separation response function (Figure 3, 4, 5) predicted optima at 9.824%, 8.055%, 8,055% acetonitrile in eluent. Predicted retention times for a computer - simulated chromatographic run, with optimum concentration of acetonitrile provided by the use of these three criteria, is shown in Table 2.

CONCLUSIONS

Because all criteria have advantages and disadvantages, it is recommended that, in practice, two different criteria be used. The results than will be complementary and the better criteria can be selected as appropriate for a particular analysis. The criteria minimum t_R difference provides information about peak and its neighbour, so there can be seen direct influence of a particular chromatographic parameter on separation of two neighbour peaks. This information is very useful for analysis of a sample, which does not have a great difference in concentration of components. On the contrary, criteria Δt_R product, separation factor, and multipeak separation response function, has the advantage of taking all of the peaks into account at the same time, so, they can provide information about whole analytical system. Which of these three criteria will be chosen for double criteria optimisation depends, first, on the separation of two least separated peaks and second, on time of the chromatographic run. The criteria which provides the biggest separation between two least separated peaks and the shortest analysis time will be chosen. For these purposes the computer - simulated chromatogram is designed (Table 2). General recommendations for double criteria optimisation of separation in ion chromatography are minimum t_R difference criteria and multipeak separation response function.

REFERENCES

1. P. Dasgupta, Anal. Chem., **64(15)**, 775A-/83A (1992).

2. J. D. Glajc, J. J. Kikland, J.Chromatogr., **485**, 51-63 (1989).

3. J. E. Madden, P. R. Haddad, J. Chromatogr**.**, **850(1-2)**,29–41 (1999).

4. P. Hajos, O. Horvath, V. Danke, Anal. Chem. **67**, 434–441 (1995).

5. T. Safni Takeuchi, T. Miwa, Y. Hashimoto, H. Moriyama, J. Chromatogr. **850(1-2)**, 65-72 (1999).

6. G. Kura, J. Chromatogr., **644**, 198-201 (1993).

7. D. R. Jenke, J. Chromatogr. Sci., **34**, 394-398 (1996).

8. L. G. Sabate, X. Tomas, J. High Resol. Chromatogr. Commun, **7**, 104-6 (1984).

9. B. J. M. De Spiegeleer, P. H. M. De Meloose, G. A. S. Seghers, Anal.Chem., **59**, 62–64 (1997).

10. S. Babić, M. Petrović, M. Kaštelan-Macan, Optimizacija kromatografskog razdvajanja pesticida, Kem. Ind.,**47**, 275-279 (1998).

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