



**Institute for Advanced Studies
in Basic Sciences**
Gava Zang, Zanjan, Iran

Calculation and Meaning of Feasible Band Boundaries in Multivariate Curve Resolution of a Three-Component System

Ph.D. Thesis

Samira Beyramysoltan

**Supervisors: Prof. H. Abdollahi
Prof. R. Rajkó**

January 2014

Acknowledgment

It is not so vague that the success of any project depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who have been instrumental in the successful completion of this project.

I would like to start with the person who motivates me in doing this project, my supervisor Prof. Hamid Abdollahi. I would like to express my deep and sincere gratitude to him for the continuous support of my Ph.D. study and research, and for all I learned from his immense knowledge. Thanks him for questioning me about my ideas, helping me think rationally and even for hearing my problems. I wish to especially thank him for giving opportunity to cooperate with Prof. Róbert Rajkó. A special gratitude I give to Prof. Róbert Rajkó who accepted to supervise this project from the University of Szeged, Hungary. I enjoyed the personal discussion with him and the time I spent with him during nine months in Szeged. He has taught me how a person can succeed in achieving what seems impossible to begin with.

I hope the best success for my best academic family, Prof. Abdollahi and Prof. Rajkó whom taught me to constrain all of power I have for reducing the possible ambiguities in research and life ways.

I would also like to thank my committee members, Prof. Mojtaba Shamsipour, Prof. Taghi Khayamiyan, Dr. Mohamad Rafiee, and Dr. Mehdi Vasighi for serving as my committee members even at hardship. I also want to thank you for letting my defense be an enjoyable moment, and for your brilliant comments and suggestions, thanks to you.

My acknowledgement will never be complete without the special mention of Dr. Fariba Nazari for all support that she has extended to me throughout.

I also wish to acknowledge all the teachers I learnt from since my childhood, I would not have been here without their guidance, blessing and support. My special thanks to Prof. Behzad Haghighi, Dr. Mohsen Kompany-Zareh, for teaching me in my Ph. D. time. I feel privileged to be their student once, a feeling that every student of their will has.

I would like to acknowledge all of my friends for their moral support and motivation, which drives me to give my best. I find myself lucky to have friends like them in my life. Unfortunately, I cannot list all of them at this text, but they will always be safe in my heart.

Last but not the least; I would like to acknowledge the people who mean world to me, my parents, sisters, and brothers. They were always supporting me spiritually throughout my life and encouraging me with their best wishes. Special thanks to my Dad who enlightened my direction in science for first time and it is so gloomy day to me that he is not by the side of me now. Words cannot express how grateful I am to my Mum for all of the sacrifices that she has made on my behalf. Her prayer for me was what sustained me thus far.

Samira Beyramysoltan

IASBS

January 21, 2014

Abstract

The curve resolution (CR) methods attract substantial research efforts aimed to discover knowledge of multicomponent systems. The objective of soft modeling, as special part of CR methods, is to resolve a second-order bilinear data matrix into its contributing matrices without prior knowledge about the chemical or physical model of system under study. The obtained results by soft modeling multivariate curve resolution methods often are not unique and are questionable because of rotational ambiguity. It means a range of feasible solutions equally fit experimental data. Due to rotational ambiguity, the accuracy of the result of soft methods was abolished by systematic error in case of quantitative analysis. Aiming to increase the accuracy, the range of solutions can be reduced by applying the useful knowledge of the studied chemical system as constraints.

It seems when there is no unique solution for the system, consideration of all feasible solutions (comparing with one solution that can be obtained with several multivariate curve resolution methods) can provide useful information about system and process under study.

Introduction to a novel grid search method

SMCR methods method can calculate the area of the feasible regions for each component, while they are not able to detect which solutions of these feasible regions are corresponding with each other. Therefore, it is valuable to modify previous methods to develop one new method with this ability. In this study, firstly in chemometric literature, a novel grid search method is proposed. The method can provide the area of feasible solutions associated to each component and correspondence relations among solutions simultaneously.

This introduced method gives an opportunity to investigate constraints effect and to compare obtained feasible solutions by different approaches as well.

I. Investigation of the Equality Constraint Effect on the Reduction of Rotational Ambiguity in Three-Component System Using a Novel Grid search Method

Regarding to chemometric literature, a survey of useful constraints for the reduction of the rotational ambiguity is a big challenge for chemometrician. It is worth to study the effects of applying constraints on the reduction of rotational ambiguity, since it can help us to choose the useful constraints in order to impose in multivariate curve resolution methods for analyzing data sets. In this work, we have investigated the effect of equality constraint on decreasing of the rotational ambiguity. For calculation of all feasible solutions corresponding with known spectrum, a novel systematic grid search method based on Species-based Particle Swarm Optimization is proposed in a three-component system.

II. A Systematic Investigation on Meaning of Feasible Band Boundaries in Multivariate Curve Resolution of a Three-Component System

In the different studies by Abdollahi et al. and Rajko, different approaches were compared on the meaning of feasible band boundaries in MCR methods for two component system. It was considered that all approaches characterize the same feasible band boundaries in the case of a two-component system. With the same aim, to best of our knowledge firstly in the literature, grid search and MCR-Bands approaches are examined for the calculation of band boundaries of feasible solutions of a three component system. The MCR-Bands method based on exploring of the extreme values of the Signal Contribution Function (SCF) relative to the elements of the transformation matrix by a non-linear constrained optimization algorithm defines the estimated boundaries of the feasible solutions band. Aimed at evaluation of two methods in meaning of band boundaries, the SCF is calculated for all the explored feasible solutions by a grid search method based on Species Particle Swarm Optimization (SPSO) and results are displayed in appropriate mesh and contour plots. The extreme values of SCF are determined and compared with the results of MCR-Bands program.

III. Newer Developments on Analytical Self-Modeling Curve Resolution (SMCR)

Analytical SMCR methods resolve the data set to all feasible solutions using only non-negativity constraints. Lawton-Sylvester method was the first presented direct method to analyze a two-component system and it was generalized as Borgen plot for determining the feasible regions in three-component system. It seems to require the geometric view for considering curve resolution methods stopped general investigation on the Borgen work for 20 years. Then, Rajkó and Istevan revised and elucidated principles of existing theory in

SMCR methods and subsequently introduced computational geometry tools for developing an algorithm to draw Borgen plot in three-component system. Although, the analytical SMCR methods are definitely fast, but their inability in analysis of the data set with immoderate noise and in implementation of constraints limits their application. In this study, analytical SMCR methods will be described with simplest concepts and details of a developmental type of Borgen plot drawing algorithm will be given. Subsequently, for the first time in the literature, the equality and the unimodality are successfully implemented in the Lawton-Sylvester method. To end, a state-of-the-art procedure was proposed to impose equality constraint in the Borgen plot.

IV. Users' guide to *LSandBP*

Toolbox for the computation of the feasible solutions of two and three component systems using analytical SMCR methods.

A new Graphical User friendly Interface (GUI) is presented in MatLab computer program to introduce the abilities of analytical SMCR methods in resolving two-way data set to pure factors. Currently, this interface provides the direct computation of feasible regions and bands associated to components in two and three component systems using the Lawton-Sylvester and Borgen plot methods, respectively. The result can also be provided by implementing the equality and unimodality constraints in Lawton-Sylvester method and the equality constraint in Borgen plot. A prominent feature of the representation in this GUI is an interactive visual inspection of constraint effects on the feasible regions and bands.

V. Definition and Detection of Data based Uniqueness

Incorporation of some useful information may lead to drastically decreasing the ambiguity in the analysis of bilinear data sets by the curve resolution tasks. Some profiles with specific condition could be resolved uniquely under non-negativity constraint in the decomposition of a two-way data set. Uniqueness condition of minimal constraint systems (termed data based uniqueness) remains as a mysterious question in the literature. In this study, for the first in the literature, data based uniqueness is investigated in details and general procedure based on data set structure information is presented for detection of profiles in which recovered unambiguously in minimal constrained SMCR. Close inspection of local rank information and Borgen plot results lead to devise the comprehensive theorem which could be considered as a corner-stone of data based uniqueness detection.

CONTANTS

CHAPTER 1	1
1. GENERAL INTRODUCTION	1
1.1 CHEMOMETRICS	1
1.2 DATA ANALYSIS	2
1.3 FACTOR ANALYSIS.....	3
1.3.1 The Singular Value Decomposition, SVD.....	3
1.4 CURVE RESOLUTION METHOD	4
1.4.1 Soft Modeling Methods	4
1.4.1.1 Ambiguities.....	5
1.4.1.2 Constraints: Definition, Classification.....	6
Equality and Inequality Constraints Based On Chemical or Mathematical Properties	6
1.4.1.2.1 Non-negativity	7
1.4.1.2.2 Unimodality	7
1.4.1.2.3 Closure	8
1.4.1.2.4 Known Profiles	8
1.4.1.2.5 Hard-Modeling Constraints: Physicochemical Models	8
1.4.1.2.6 Local-Rank Constraints; Selectivity, and Zero Concentration Windows	9
1.4.1.2.6.1 Manne's Resolution Theorems	10
1.4.1.2.6.2 Window Factor Analysis (WFA)	11
1.4.1.2.6.3 SubWindow Factor Analysis (SWFA),.....	13
1.4.1.4 The Extent of Rotational Ambiguity.....	14
1.4.1.4.1 In Any Number of Components: MCR-Bands Method.....	14
1.4.1.4.2 In Two-Component System: Lawton-Sylvestre Method	16
1.4.1.4. 3.1 Investigating the Rotational Ambiguity in Three-Component Systems Using Grid Search.....	17
1.4.1.4.3.2 Borgen Method:	21
CHAPTER 2	26
2. HISTORICAL BACKGROUND	26

2.1 MULTIVARIATE CURVE RESOLUTION METHODS	27
2.2 EQUALITY CONSTRAINT EFFECT.....	34
2.3 DETECTION OF UNIQUE SOLUTION.....	35
CHAPTER 3.....	37
3. NUMERICAL EXPERIMENTS	37
3.1 BEER-LAMBERT'S LAW	38
3.2 GAUSSIAN CURVES	40
3.3 CONCENTRATION MODEL FOR DIPROTIC ACID IN TITRATION.....	40
3.4 Generation of Simulated Mixtures	42
3.4.1 Two-component mixtures with overlapping gaussian chromatography peak	42
3.4.2 Three-component mixtures with high overlapping in profiles	43
3.4.3 Three-component mixtures with selective properties.....	44
3.4.2.1 Three-component mixtures of chromatography systems.....	44
3.4.2.2 Three-component titration mixtures	45
3.5 SOFTWARE	48
CHAPTER 4.....	49
4. RESULTS AND DISCUSSION	49
4.1. GENERAL INTRODUCTION ON SMCR PROBLEM	49
4.1.1 Reduction in the Number of Dimensions.....	50
4.1.2 The Geometry of Abstract Space in Three-component system	51
4.2 DEFINING AREAS OF FEASIBLE SOLUTIONS BY THE GRID SEARCH METHOD	53
4.2.1 Species-based Particle Swarm Optimization (SPSO).....	56
4.2.2 Computation of Area of feasible solutions using gridsearch/SPSO	58
4.3 EFFECT OF EQUALITY CONSTRAINT ON REDUCTION OF ROTATIONAL AMBIGUITY ...	60
4.3.1. Equality constraint effect on regions of complementary components in dual	
space.....	66
4.3.2. Additional examples on Equality constraint effect.....	68
4.3.3 Conclusions.....	75
4.4 A SYSTEMATIC INVESTIGATION ON MEANING OF FEASIBLE BAND BOUNDARIES IN	
MULTIVARIATE CURVE RESOLUTION OF A THREE-COMPONENT SYSTEM.....	76
4.4.1 Visualization of Objective Function of MCR-Bands on Abstract Space	77
4.4.2 The Effect of Initial Estimations on the Results of MCR-Bands.....	83

4.4.3 Conclusion	87
4.5 NEWER DEVELOPMENTS ON ANALYTICAL SELF-MODELING CURVE RESOLUTION (SMCR).....	88
4.5.1 Lawton-Sylvester method	89
4.5.1.1 To Implement the Constraints in Lawton-Sylvester Method.....	91
4.5.1.1.1 To impose the equality constraint	91
4.5.1.1.2 To impose the unimodality constraint.....	92
4.5.2 New Algorithm for Borgen plot.....	95
4.5.2.1 Introduction to Geometry of Abstract Space in Borgen	95
4.5.2.2 Algorithm Steps in Borgen Drawing	96
4.5.2.3 Computation of the Area of Feasible solutions for a Special Data Set.	102
4.5.3 To Implement the Equality Constraint in Borgen plot.....	104
4.5.4 Conclusions.....	109
4.6 USER'S GUIDE TO LSANDBP	110
4.6.1 Overview to LSandBP Method	111
4.6.1.1 A Screen-Shot of the LSandBP GUI	111
4.6.1.2 Execution of LSandBP Program.....	112
4.6.1.2.1 Comparison of the Screens of GUI after Loading Two and Three Components System.....	116
4.6.1.3 Implementing the Constraints in GUI.....	118
4.6.1.3.1 Implementing the Unimodality Constraint in GUI.....	118
4.6.1.3.1 Implementing the Equality Constraint in GUI.....	119
4.6.1.4 Educational Aims in GUI.....	122
6.1.4.1 Optional Panel in GUI	123
4.6.1.4.2 Locking the left button of mose to select a point on the axes to introduce known profiles to GUI	124
4.6.2 Conclusion	126
4.7 DEFINITION AND DETECTION OF DATA BASED UNIQUENESS	127
4.7.1 Theoretical Background.....	128
4.7.2 Numerical Experiment	132
4.7.3 Investigation of possible data based uniqueness cases in three-component systems.....	132
4.7.4 Presentation the Schematic of Possible Abstract Spaces for the Spectrophotometry Data Sets.....	146

4.7.5 Conclusions..... 154

List of Figures

- Figure 1.1** Recovery of the concentration profile of the n th compound by window factor analysis. (a) SVD on the raw data matrix and determination of the concentration window, \mathbf{R} (steps 1 and 2); (b) SVD on the matrix formed by suppression of the concentration window of the n th component, \mathbf{R}_0 (step 3); (c) recovery of the part of the spectrum of the n th component orthogonal to all the spectra in \mathbf{R}_0 , $\mathbf{V}_n^{\perp 0}$ (step 4); and (d) recovery of the concentration profile of the n th component (step 5). 12
- Figure 1.2** Application of SubWindow Factor Analysis (SWFA) for resolution. (a) Concentration profiles of A, B, and C and subwindows used for the resolution of component B (first containing A and B compounds and second containing B and C compounds). (b) The A,B plane is defined by the pure spectra of A and B (\mathbf{s}_A , \mathbf{s}_B) and the plane B,C by the pure spectra of B and C (\mathbf{s}_B , \mathbf{s}_C). The intersection of both planes must be necessarily the pure spectrum of B. 13
- Figure 1.3** Determination of feasible bounding profiles investigated and published by Lawton and Sylvestre^{12a}: PC1-PC2 plot: the numbered points given by normalization and factorization of the original data represent the spectral profiles and should fall into the straight line. The bounds can be given by the intersection of solid and broken lines with scores line. 16
- Figure 1.4** Three-dimensional representation of ssq as a function of the elements x_2 and x_3 ; three areas of feasible solutions are revealed. See the Numerical Experiments section for details on the data used to generate this graph. 20
- Figure 1.5** The three feasible regions (shadowed areas) according to the three components that are the transformed true profiles should be positioned in those regions. The dashed dotted lines form the two Borgen simplexes (i.e. triangles). The feasible regions are their appropriate sections with the complete limiting function, which is marked with solid tick line. 21
- Figure 3.1** Pure concentration (\mathbf{C} , 3.1a), spectral profiles (\mathbf{S} , 3.1b) and surface plot of the simulated HPLC-DAD data (\mathbf{R} , 3.1c) of multiplication of \mathbf{C} by \mathbf{S} . 42
- Figure 3.2** Pure concentration (\mathbf{C} , 3.2a), spectral profiles (\mathbf{S} , 3.2b) and simulated HPLC-DAD data (\mathbf{R} , 3.2c) of multiplication of \mathbf{C} by \mathbf{S} . The data set generated by 0.3% noise level (\mathbf{R} , 3.2d). 43
- Figure 3.3** Pure concentration (\mathbf{C} , 3.3a), spectral profiles (\mathbf{S} , 3.3b) and simulated HPLC-DAD data (\mathbf{R} , 3.3c) of multiplication of \mathbf{C} by \mathbf{S} . 43
- Figure 3.4** True concentration (\mathbf{C} , 3.4a), spectral profiles (\mathbf{S} , 3.4b) and simulated data sets (\mathbf{R} , 3.4c) of multiplication of \mathbf{C} by \mathbf{S} in the simulated cases. 47

- Figure 4.2.1** Illustration of the obtained results by the optimization method in one iteration of the grid search method. (The x_1 , y_1 display labels of x-axis and the x_2 , y_2 are labels of y-axis in two plots. The x_1 and x_2 are the coordinates resulting of the projection of row vectors in the spectral space; y_1 and y_2 depict the coordinates of the projected column vectors in the concentration space) 55
- Figure 4.2.2** Depiction of complementary solutions with the coordinates of known profile in a three-component system. 56
- Figure 4.2.3** The obtained feasible solutions using the proposed method under non-negativity constraint for noisy and noiseless data sets, The colored lines relate to the boundaries of solutions obtained under non-negativity constrain; dashed and solid lines display this solutions for noisy data and noiseless data, respectively. a: spectral solutions, b: concentration solutions. In both cases (a, b) left panels show the obtained areas of feasible solutions and right panels display the translated profiles of feasible regions. 59
- Figure 4.3.1** The obtained feasible solutions for data sets with different noise levels (0, 0.3% of maximum magnitude of absorbance) using the proposed method. a: Range of feasible spectral profiles, b: Range of feasible concentration profiles. The colored lines relate to the boundaries of solutions obtained under non-negativity constrain; dashed and solid lines display this solutions for noisy data and noiseless data, respectively. The colored areas display solutions obtained under non-negativity and equality constraints (the spectrum of the first component is supposed as known spectrum). The area with light color is associated to noisy data whereas the areas with dark color display the solutions for noiseless data set. Feasible bands also were shown in the same way as well. 62
- Figure 4.3.2** A graphical model for the representation of relation between fixed point in spectral space and the deduced line in concentration space. The colorful stars depict the coordinates of true profiles in abstract space as one obtained feasible solution when equality constraint was imposed, the dashed black lines demonstrate a triangle which is created by true profiles. Blue star shows the coordinates of known spectrum and the red line in concentration space is the restricted space corresponding to known spectrum. 65
- Figure 4.3.3** The representation of the relation between fixed point in spectral space and the deduced line in concentration space in case of a data set with moderate noise (noise level is 0.3% of maximum magnitude of data). 68
- Figure 4.3.4** Representation of the constructed concentration and spectral profiles that used for making first example. For the generating of these profiles, the obtained feasible solutions of analysis of previous data are used. a: constructed spectral profiles (right panel) and the position of these profiles in concentration space (left panel), b: translated concentration profiles (right panel) and the coordinates of these profiles in spectral space (left panel). Dashed line and yellow stars display the formed triangle by this feasible solution in concentration and spectral space. 69

Figure 4.3.5 The simulated data set of the concentration and spectral profiles displayed in Figure 4.3.4, and its corresponding concentration and spectral abstract space calculated using MCR methods. As this figure shows obtained data set and abstract spaces are exactly same with the displayed data set and abstract space in the mentioned example in the manuscript. It is a trivial case, because for the constructing of the concentration and spectral profiles, here, the feasible solutions of the first example were used. It should remember that feasible solutions of one data set have different shape causes by rotational ambiguity but, they will be result in the same data set and abstract spaces. 69

Figure 4.3.6 The obtained feasible solutions for the first example using the proposed method under non-negativity and equality constraints; where the spectrum of third component is supposed as known spectra. For best observation these results were shown on the obtained feasible solution under non-negativity constraint. a: Range of feasible spectral profiles, b: Range of feasible concentration profiles; white areas with colored boundary relate to solutions obtained under non-negativity constraint, while the colored areas display solutions obtained under non-negativity and equality constraints. Feasible bands also were shown in a same way as well. 70

Figure 4.3.7 Representation of the constructed concentration and spectral profiles that used for making the second example. a: constructed spectral profiles (right panel) and the position of these profiles in concentration space (left panel), b: translated concentration profiles (right panel) and the coordinates of these profiles in spectral space (left panel). Dashed line and yellow stars display the formed triangle by this feasible solution in the concentration and spectral space. Figure 4.3.5 shows the data set and abstract space of this example. 71

Figure 4.3.8 The obtained feasible solutions for the second example using the proposed method under non-negativity and equality constraints; where the spectrum of third component is supposed as known spectra. a: Range of feasible spectral profiles, b: Range of feasible concentration profiles; white areas with colored boundary relate to solutions obtained under non-negativity constraint, while the colored areas display solutions obtained under non-negativity and equality constraints. Feasible bands also were shown in the same way as well. 72

Figure 4.3.9 Representation of the constructed concentration and spectral profiles that used for making third example. a: constructed spectral profiles (right panel) and the position of these profiles in concentration space (left panel), b: translated concentration profiles (right panel) and coordinates of these profiles in spectral space (left panel). Dashed line and yellow stars display the formed triangle by this feasible solution in concentration and spectral space. Figure 4.3.5 shows the data set and abstract space of this example. 73

Figure 4.3.10 The obtained feasible solutions for the third example using the proposed method under non-negativity and equality constraints; where the spectrum of third component is supposed as known spectra. a: Range of feasible spectral profiles, b: Range of feasible concentration profiles; white areas with colored boundary relate to solutions obtained under non-negativity constraint, while the colored areas display solutions obtained under non-negativity and equality constraints. Feasible bands also were shown in the same way as well. 74

Figure 4.4.1 The figure illustrates the computation of SCF value for every feasible solution of one component.	79
Figure 4.4.2 A graphical image of the volume of SCF values in mesh plots that they calculated by the grid search method, a: Concentration abstract space, b: Spectral abstract space.	81
Figure 4.4.3 The estimated band boundaries by grid search method, a: Concentration feasible solutions, b: Spectral feasible solution, the yellow and pink points show the coordinates of lower and upper estimated band boundaries in abstract space, respectively. The obtained band boundaries displayed using yellow and pink dashed lines on feasible band.	82
Figure 4.4.4 The demonstration of MCR-Bands result when true profiles used as initial estimation, a: Spectral feasible solutions, b: concentration feasible solution, the yellow and pink points show the coordinates of lower and upper estimated band boundaries in abstract space, respectively. The obtained band boundaries display with yellow and black dashed lines on feasible band.	84
Figure 4.4.5 Initial estimation used in MCR-Bands method which it is chosen from SMCR solutions.	85
Figure 4.4.6 The maximum surface of SCF values volume related to second component's concentration feasible region, the image show the existence of maxima in this SCF values volume.	86
Figure 4.5.1 An illustration of Lawton-Sylvester plot for the two-component system. a: depiction of limiting lines outlining the inner boundaries (red dashed-point lines) and the outer boundaries (pink lines); blue lines indicate the no-negative lines starting from the origin and dark blue dashed line involves the coordinates of response vectors, b: a Lawton-Sylvester plot for two component system, red and green vertical line display the identified feasible regions corresponding with two components.	89
Figure 4.5.2 a and b show the feasible solutions of the data set in concentration and spectral spaces, respectively.	90
Figure 4.5.3 The figure displays the result of analysis of HPLC-DAD data set (Figure 3.1c) using Lawton-Sylvester method under equality constraint when the spectral profile of the second component is known. a: a schematic of the algorithm of imposing the equality constraint in Lawton-Sylvester method. b and c show the feasible solutions affected by the equality constraint in concentration and spectral spaces, respectively.	92
Figure 4.5.4 The figure displays the result of analysis of HPLC-DAD data set (Figure 2c) using Lawton-Sylvester method under unimodality constraint a: a schematic of steps 2 and 3 in the algorithm of imposing the unimodality constraint in Lawton-Sylvester method, b: concentration feasible solutions, c: spectral feasible solutions.	94

Figure 4.5.5	The geometrical demonstration of the abstract space in a three-component system.	96
Figure 4.5.6	a: Illustration of outer polygon computation procedure in Borgen plot. Plot shows the sides of inner polygon in spectral space define the coordinates of vertices of outer polygon. The duality correspondence between a side of inner polygon (pink line) in spectral space and a vertex of outer polygon in concentration is represented by pink double arrow. b: Borgen triangles and permitted regions for the feasible region of components determined by simplex rotation algorithm; sides of Borgen triangles are shown with dashed lines, while the vertices of triangles with numbered points; the feasible parts of outer polygon are displayed with light green color.	98
Figure 4.5.7	A three-component HPLC-DAD data set and the result of its resolution using Borgen plot. a: true concentration profiles (C), b: true spectral profiles (S), c: the data set generated from C and S , d: concentration solutions, b: spectral solutions. In both cases (d, e) left panels show the obtained areas of feasible solutions and right panels display the translated profiles of feasible regions.	102
Figure 4.5.8	A three-component HPLC-DAD data set with possibility of unique resolution of one profile under minimal information. a: true concentration profiles, b: spectral profiles, c: the simulated HPLC-DAD data. d: feasible solutions of the data set in concentration space, e: the determined spectral feasible solutions.	103
Figure 4.5.9	Demonstrates the steps of imposing the equality constraint in Borgen plot.	107
Figure 4.5.10	Final representation of applying equality constraint.	108
Figure 4.6.1	GUI windows of the LSandBP program.	111
Figure 4.6.2	GUI window of the LSandBP program after loading a two-component system.	112
Figure 4.6.3	GUI windows of the LSandBP program after loading a three-component system.	113
Figure 4.6.4	GUI window of LSandBP program after changing the option of result demonstration in GUI window shown in Figure 4.6.2.	115
Figure 4.6.5	Creating the same plot outside of the GUI screen by the mouse right click on the plot.	116
Figure 4.6.6	Illustration of non-negativity lines in feasible regions by pushing the "lines for non-negativity constraint" button in GUI window shown in Figure 4.6.2.	117
Figure 4.6.7	Feasible solution obtained from imposing the unimodality constraint on concentration profile of component 2.	119

Figure 4.6.8 Feasible solution obtained from imposing the equality constraint in Lawton-Sylvester method when spectral profile of component 1 is known.	120
	121
Figure 4.6.9 Feasible solution obtained from imposing the equality constraint in Borgen plot when the spectral profiles of components 1, 2 are known.	
Figure 4.6.10 laying the profiles and their coordinate on the plots, yellow points in feasible regions and white lines in feasible bands show the position of simulated concentration profiles on feasible region and band in GUI.	122
Figure 4.6.11 Feasible solutions (4.6.11b) obtained from imposing the equality constraint when a point (4.6.11a) is selected from the feasible region.	125
Figure 4.7.1 A schematic of feasible space associated to a three-component system.	128
Figure 4.7.2 An illustration of abstract space of a data set with a unique profile.	130
Figure 4.7.3 Visualization of the geometry of abstract spaces in U-space (a), in V-space (b) for case I. c and d: illustrate columns and rows of data matrix which are located on outer polygon to define the fixed subspace for interfering compounds (components 1, 2) of unique profile (components 3) in V-space. e and f: show feasible concentration (C), spectral profiles (S) which generate the data set case I (Figure 3.4c-case I). The horizontal lines whose have the same color with profiles of components display the window of presence of components.	134
Figure 4.7.4 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space for case (II-a). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components.	136
Figure 4.7.5 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space for case (II-b). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components.	137
Figure 4.7.6 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space for case (III-a). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components.	139
Figure 4.7.7 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space for case (III-b). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components.	140
Figure 4.7.8 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space, for case (IV-a). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components.	142

Figure 4.7.9 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space, for case (IV-b). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components. 143

Figure 4.7.10 Visualization of the geometry of abstract spaces and feasible bands a: in concentration space, b: in spectral space, for case (V). In feasible bands plot, the horizontal lines whose have the same color with profiles of components display the window of presence of components. 144

List of Schemes

Scheme 1.1 An illustration of grid search algorithm in three-component system	19
Scheme 1.2 An illustration of tangent and simplex rotation in Borgen algorithm ⁵⁹	22
Scheme 3.1 Diagram demonstrating Beer-Lambert absorption of a beam of light as it travels through a cuvette of size l containing solution of concentration c and molar absorptivity ϵ .	38
Scheme 3.2 Diagram demonstrates decomposition of spectra \mathbf{R} into corresponding concentration (\mathbf{C}) and absorptivity (\mathbf{S}) matrices. The matrix \mathbf{E} is representative of the experimental noise associated with any real measurement.	39
Scheme 4.1.1 a: Illustration of a feasible solution in a three-component system. b: Depiction of complementary solutions with the coordinates of spectral profile in a three-component system.	52
Scheme 4.2.1 A schematic of SPSO algorithm.	57
Scheme 4.5.1 The algorithm determining the complete limiting curve. The lines and points are marked with L and P respectively. The green line is the feasible parts on outer polygon are related to the component which its limiting curve should be recovered. The magenta lines mark the feasible solutions of complementary components on outer polygon.	100