

Simplex Optimization and Its Applicability for Solving Analytical Problems

Anna Maria Michałowska-Kaczmarczyk¹, Tadeusz Michałowski^{2*}

¹Department of Oncology, The University Hospital in Cracow, Cracow, Poland

²Faculty of Engineering and Chemical Technology, Cracow University of Technology, Cracow, Poland

Email: michalot@o2.pl

Received 14 April 2014; revised 14 May 2014; accepted 21 May 2014

Copyright © 2014 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Formulation of the simplex matrix referred to n - D space, is presented in terms of the scalar product of vectors, known from elementary algebra. The principles of a simplex optimization procedure are presented on a simple example, with use of a target function taken as a criterion of optimization, where accuracy and precision are treated equally in searching optimal conditions of a gravimetric analysis.

Keywords

Simplex, Simplex Optimization Procedure

1. Introduction

Simplex is a geometric figure, formed on the basis of $n+1$ points A_i ($i=0, \dots, n$) in the n -dimensional space, *i.e.*, a number of the points exceeds the dimension of the space by one. These points are referred to as the vertices of the simplex. Distribution of the points A_i in this space is represented by a matrix of this simplex. Specifying the coordinates for A_i is easy if it concerns the 2- D or 3- D space, but it becomes less comprehensible when the issue concerns the n -dimensional (n - D) simplex. Although in the literature [1] one can find ready-made forms of the simplex matrix in n - D space, but information on how to receive it in an easy manner is lacking.

The simplex concept is the basis for the Nelder-Mead [2] simplex optimization procedure (SOP) [3], conceived as a modification of the simplex method of Spendley, Hext and Himsworth [4]. The SOP is easy to use, and does not require calculation of derivatives [5] [6], as in the gradient (local steepest descent) method [7] [8]). The SOP

*Corresponding author.

is widely applicable and popular in different fields of chemistry, chemical engineering, and medicine [9]. Furthermore, it works well in practice on a wide variety of problems, where real-valued minimization functions with scalar variables are applied.

The sequential simplex method is considered as one of the most effective and robust methods applied in methodology of Evolutionary Operation (EVOP) experimental design [10]-[15]. The SOP method was implemented in MINUIT (a Fortran from CERN [16] package), then in Pascal, Modula-2, Visual Basic, and C++ [17]. The iterations are stopped when the function minimized is less than a preset value.

In this article, the problem of obtaining the simplex matrix in n - D space will be presented on the basis of the triangle and the scalar product concept, well-known to the students from earlier stages of education. The evolution of the simplex according to SOP [3] [18] will also be presented in a understandable manner.

2. Simplexes in 2- D and 3- D Space

In order to introduce the simplex concept, we start from the point (0- D), (I) segment (1- D), (II) equilateral triangle (2- D), and (III) tetrahedron (3- D) concepts, known from the elementary geometry. The 0- D , 1- D , 2- D , 3- D (and generally n - D) notations express the dimensionality of the corresponding geometrical entities (Figure 1).

The points: A_0, A_1, A_2 are vertices of the triangle $A_0A_1A_2$; the points: A_0, A_1, A_2, A_3 are the vertices of the tetrahedron $A_0A_1A_2A_3$. A_0A_1 is one of the edges of the triangle; A_0A_1 is one of the edges of the tetrahedron. Equilateral triangle $A_0A_1A_2$ is one of walls of the tetrahedron.

Segment, equilateral triangle, and tetrahedron can be presented in the same scale; it means that all distances, equal to unity (chosen arbitrarily), between the (neighbouring) points A_i and A_j of a polygon are assumed, *i.e.* the length $|A_iA_j| = 1$.

All angles between edges of the equilateral triangle are equal to 60° ($\pi/3$ rd). All angles between adjacent tetrahedron edges are equal 60° too, owing to the fact that all the tetrahedron walls are composed of equilateral triangles (2- D). By turns, tetrahedrons form the 3- D walls in 4- D polygon, etc. It means that all angles between adjacent edges of a symmetrical n - D polygon are equal 60° , as well.

The equilateral triangle can assume different positions on the plane. A particular case is the triangle with unit edges, "anchored" at the origin of co-ordinate axis, as one presented in Figure 2.

The successive vertices of the equilateral triangle can be presented in matrix form, where the rows are expressed by co-ordinates of the corresponding points A_i ($i = 0, 1, 2$):

$$\mathbf{X} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \\ 1/2 & \sqrt{3}/2 \end{bmatrix} \begin{matrix} A_0 \\ A_1 \\ A_2 \end{matrix} \quad (1)$$

The second and third rows of this matrix are identical with components of transposed vectors: A_0A_1 and A_0A_2 , respectively:

$$A_0A_1 = [1, 0]^T, \quad A_0A_2 = [1/2, \sqrt{3}/2]^T$$

The tetrahedron can assume different positions in 3- D space. A particular case is the tetrahedron anchored at the origin of co-ordinate axis as one presented in Figure 3.

The successive vertices of the tetrahedron can be presented in the matrix form:

$$\mathbf{X} = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 1/2 & \sqrt{3}/2 & 0 \\ 1/2 & \sqrt{3}/6 & \sqrt{6}/3 \end{bmatrix} \begin{matrix} A_0 \\ A_1 \\ A_2 \\ A_3 \end{matrix} \quad (2)$$

The second, third and fourth rows of this matrix are identical with components of the transposed vectors: A_0A_1 , A_0A_2 and A_0A_3 , respectively:

$$A_0A_1 = [1, 0, 0]^T; \quad A_0A_2 = [1/2, \sqrt{3}/2, 0]^T; \quad A_0A_3 = [1/2, \sqrt{3}/6, \sqrt{6}/3]^T$$

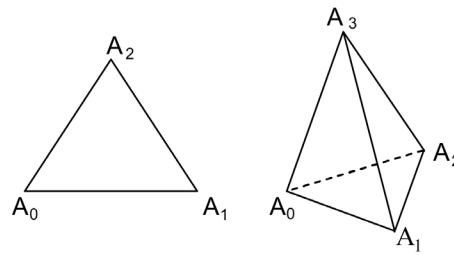


Figure 1. Equilateral triangle and tetrahedron.

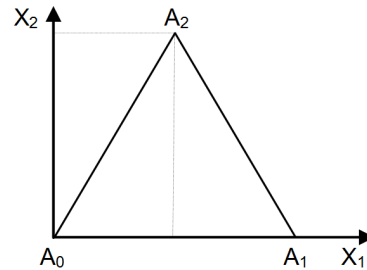


Figure 2. The equilateral triangle with unit edges and points: $A_0(0,0)$; $A_1(1,0)$; $A_2(0.5, \sqrt{3}/2)$.

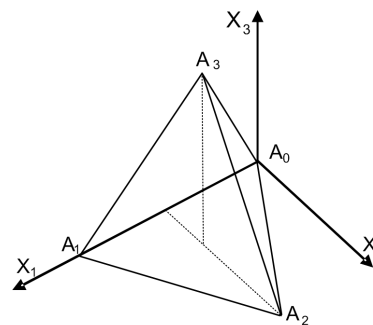


Figure 3. The tetrahedron with unit edges and $A_0(0,0,0)$; $A_1(1,0,0)$; $A_2(1/2, \sqrt{3}/2, 0)$; $A_3(1/2, \sqrt{3}/6, \sqrt{6}/3)$.

3. Simplexes in n - D Space

The segment, equilateral triangle and tetrahedron are imaginable concepts. However, application of the concepts involved with geometric figures of higher dimension ($n \geq 4$) is beyond imagination. One should be taken into account that, in the simplex optimization, we are forced, as a rule, to consider higher number of factors influencing the optimizing process.

Although the figures in n - D space (Cartesian co-ordinate system) are beyond imagination, one can present them in projective space. In **Figure 4**, any pair of points of the simplex is connected, informally, by a segment (line); the segments (sides, edges) are marked there with broken lines. Particularly, two points form the 1- D simplex in 1- D space. Adding a third point (that not lies along the segment or its extension) gives a triangle (2- D simplex) in 2- D space. Adding a fourth point in 3- D space (not coplanar with 2- D simplex plane), one obtains a tetrahedron (3- D simplex), etc. Generally, adding a successive $k+1$ -th ($k=2,3,\dots,n-1$) point, do not lying in surface formed by $k-1$ - D simplex, one obtains the k - D simplex. In other words, adding the successive point that not lies on (or in plane of) simplexes of lower dimension and connecting it, every time, with the remaining points, one can imagine the simplexes with larger and larger dimensions, in projective space.

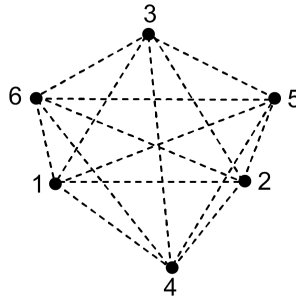


Figure 4. Formation of consecutive dimensions (up to 5- D) of a simplex in projective space.

Let us assume that the polygon is “anchored” in n - D -space in such a manner that A_0 is in the origin of the co-ordinate axis and any successive point “enters” the new dimension of the n - D -space, see **Figure 4**. It means that the co-ordinates of the corresponding points of n - D polygon are as follows:

$$A_0 = (0, 0, 0, \dots, 0, 0); A_1 = (x_{11}, 0, 0, \dots, 0, 0); A_2 = (x_{21}, x_{22}, 0, \dots, 0, 0); A_3 = (x_{31}, x_{32}, x_{33}, \dots, 0, 0); \dots; \tag{3}$$

$$A_{n-1} = (x_{n-1,1}, x_{n-1,2}, x_{n-1,3}, \dots, x_{n-1,n-1}, 0); A_n = (x_{n1}, x_{n2}, x_{n3}, \dots, x_{n,n-1}, x_{nn}).$$

This means that $x_{ij} = 0$ for $j > i$.

As stated above, the number of vertices exceeds, by 1, the dimension of the space; it means that the polygon in n - D space involves $n + 1$ vertices.

We consider a pencil of n unit vectors, $\mathbf{x}_i = A_0 A_i = [x_{i1}, x_{i2}, x_{i3}, \dots, x_{ii}, \dots, x_{in}]^T$, all starting from the point $A_0 = (0, \dots, 0)$, *i.e.*, origin of co-ordinates of n - D space and ending at the points A_i ($i = 1, 2, \dots, n$). One should notice that the basic components x_{ij} of the vector \mathbf{x}_i starting at the origin of co-ordinates, are identical with co-ordinates of the point $A_i = (x_{i1}, x_{i2}, x_{i3}, \dots, x_{ij}, \dots, x_{in})$. Then for the vectors $A_0 A_i$ based on the points specified in (3) we have:

$$\mathbf{x}_1 = A_0 A_1 = [x_{11}, 0, 0, \dots, 0]^T;$$

$$\mathbf{x}_2 = A_0 A_2 = [x_{21}, x_{22}, 0, \dots, 0]^T;$$

$$\mathbf{x}_3 = A_0 A_3 = [x_{31}, x_{32}, x_{33}, 0, \dots, 0]^T;$$

$$\mathbf{x}_i = A_0 A_i = [x_{i1}, x_{i2}, x_{i3}, \dots, x_{ii}, 0, \dots, 0]^T;$$

$$\mathbf{x}_n = A_0 A_n = [x_{n1}, x_{n2}, x_{n3}, \dots, x_{ni}, \dots, x_{nn}]^T.$$
(4)

Let us construct the matrix \mathbf{X} (Equation (5)) composed of the co-ordinates of the corresponding points in n - D space:

$$\mathbf{X} = \begin{bmatrix} 0 & 0 & 0 & \dots & 0 & \dots & 0 & 0 \\ x_{11} & 0 & 0 & \dots & 0 & \dots & 0 & 0 \\ x_{21} & x_{22} & 0 & \dots & 0 & \dots & 0 & 0 \\ x_{31} & x_{32} & x_{33} & \dots & 0 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ x_{i1} & x_{i2} & x_{i3} & \dots & x_{ii} & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ x_{n-1,1} & x_{n-1,2} & x_{n-1,3} & \dots & x_{n-1,i} & \dots & x_{n-1,n-1} & x_{n-1,n} \\ x_{n1} & x_{n2} & x_{n3} & \dots & x_{ni} & \dots & x_{n,n-1} & x_{nn} \end{bmatrix} \begin{matrix} A_0 \\ A_1 \\ A_2 \\ A_3 \\ \dots \\ A_i \\ \dots \\ A_{n-1} \\ A_n \end{matrix} \tag{5}$$

Moreover, we assume non-negative values for the coordinates, *i.e.* $x_{ij} \geq 0$, and then the elements of the ma-

trix $X = [x_{ij}]$ can be specified as follows:

$$x_{ij} = \begin{cases} > 0 & \text{for } i \geq j \\ 0 & \text{for } i < j \text{ (} i, j \in \{1, \dots, n\} \text{)} \\ 0 & \text{for } i = 0 \text{ (} j = 1, \dots, n \text{)} \end{cases} \quad (6)$$

Let e_i be the unit vector along the i -th axis, X_i , *i.e.* $|e_i| = 1$. The e_j vectors form a set of mutually orthogonal vectors in n - D space. The scalar products:

$$e_i \cdot e_j = |e_i| \cdot |e_j| \cdot \cos(\angle e_i, e_j) = \delta_{ij} = \begin{cases} 1 & \text{for } j = i \\ 0 & \text{for } j \neq i \end{cases} \quad (7)$$

where δ_{ij} is the Kronecker symbol.

Any vector x_i in n - D space can be also written as $x_i = [x_{i1}, x_{i2}, \dots, x_{in}]^T$; $x_i = \sum_{k=1}^n e_k \cdot x_{ik}$. Then the scalar product of two vectors, x_i and x_j , in n - D space is as follows:

$$x_i \cdot x_j = |x_i| \cdot |x_j| \cdot \cos(\angle x_i, x_j) = \sum_{k=1}^n x_{ik} x_{jk} \quad (8)$$

where $\angle x_i, x_j$ is the angle between vectors x_i and x_j spanning the simplex in n - D space. The angle between different vectors $x_i = A_0 A_i$ and $x_j = A_0 A_j$ of n - D simplex equals $\pi/3$ [rd], *i.e.* $\angle x_i, x_j = 60^\circ$ and then $\cos(\angle x_i, x_j) = \cos 60^\circ = 1/2$, for any pair of the vectors x_i and x_j : in triangle (2 - D), in tetrahedron (3 - D), \dots . Moreover, $\angle x_i, x_i = 0$ and then $\cos(\angle x_i, x_j) = \cos 0^\circ = 1$. If the unit vectors x_i ($i = 1, \dots, n$) are assumed, *i.e.*, $|x_i| = x_i = 1$, then from (8) and (4)-(6) we have:

$$\sum_{k=1}^n x_{ik} x_{jk} = \sum_{k=1}^m x_{ik} x_{jk} = \frac{1}{2} \text{ where } m = \min(i, j) \quad (9)$$

$$\sum_{j=1}^i x_{ij}^2 = 1, \text{ where } i = 1, \dots, n \quad (10)$$

From (9), (10) and (6) we get, by turns,

$$x_{11}^2 = 1 \rightarrow x_{11} = 1 = \left(\frac{1+1}{2 \cdot 1}\right)^{1/2} = h_1$$

$$x_{11} \cdot x_{i1} + 0 \cdot x_{i2} + \dots + 0 \cdot x_{ii} + 0 \cdot 0 + \dots + 0 \cdot 0 = \frac{1}{2}, \text{ i.e.}$$

$$x_{11} \cdot x_{i1} = 1/2 \text{ (for } i = 2, \dots, n) \rightarrow x_{i1} = \frac{1}{2} = \frac{1}{1+1} \cdot h_1 \text{ (for } 2 \leq i \leq n)$$

$$x_{21}^2 + x_{22}^2 = 1 \rightarrow x_{22} = (1 - x_{21}^2)^{1/2} = \left(1 - \left(\frac{1}{2}\right)^2\right)^{1/2} = \frac{\sqrt{3}}{2} = \left(\frac{2+1}{2 \cdot 2}\right)^{1/2} = h_2$$

$$x_{21} \cdot x_{i1} + x_{22} \cdot x_{i2} = \frac{1}{2} \rightarrow x_{i2} = \frac{1 \cdot \sqrt{3}}{3 \cdot 2} = \frac{1}{2+1} h_2 \text{ (for } 3 \leq i \leq n)$$

$$x_{31}^2 + x_{32}^2 + x_{33}^2 = 1 \rightarrow x_{33} = (1 - x_{31}^2 - x_{32}^2)^{1/2} = \frac{\sqrt{6}}{3} = \left(\frac{3+1}{2 \cdot 3}\right)^{1/2} = h_3$$

$$x_{31} \cdot x_{i1} + x_{32} \cdot x_{i2} + x_{33} \cdot x_{i3} = \frac{1}{2} \rightarrow x_{i3} = \frac{1 \cdot \sqrt{6}}{4 \cdot 3} = \frac{1}{3+1} h_3 \text{ (for } 4 \leq i \leq n)$$

$$x_{41}^2 + x_{42}^2 + x_{43}^2 + x_{44}^2 = 1 \rightarrow x_{44} = (1 - x_{41}^2 - x_{42}^2 - x_{43}^2)^{1/2} = \frac{\sqrt{10}}{4} = \left(\frac{4+1}{2 \cdot 4}\right)^{1/2} = h_4$$

$$x_{41}x_{i1} + x_{42}x_{i2} + x_{43}x_{i3} + x_{44}x_{i4} = \frac{1}{2} \rightarrow x_{i4} = \frac{1\sqrt{10}}{5 \cdot 4} = \frac{1}{4+1}h_4 \quad (\text{for } 5 \leq i \leq n)$$

and so forth. On this basis, one can write:

$$x_{jj} = h_j = \left(\frac{j+1}{2j}\right)^{1/2} \quad (\text{for } 1 \leq j \leq n) \tag{11}$$

$$x_{ij} = r_j = \frac{1}{j+1}\left(\frac{j+1}{2j}\right)^{1/2} = \left(\frac{1}{2j(j+1)}\right)^{1/2} \quad (\text{for } j < i \leq n) \tag{12}$$

The elements x_{ij} of the matrix $X = [x_{ij}]$ (Equation (5)) are thus derived with use of principles of elementary algebra and geometry. Then the n - D simplex can be written in the form

$$X = \begin{bmatrix} 0 & 0 & 0 & \dots & 0 \\ h_1 & 0 & 0 & \dots & 0 \\ r_1 & h_2 & 0 & \dots & 0 \\ r_1 & r_2 & h_3 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ r_1 & r_2 & r_3 & \dots & h_n \end{bmatrix} \tag{13}$$

One can notice that h_j (Equation (15)) is the height of j - D symmetrical simplex and r_j (Equation (16)) is the radius of j - D sphere (for $j=2$ —circle, for $j=3$ —“normal” sphere) inscribed in j - D simplex. Moreover, we have the relations:

$$h_j = r_j + R_j \text{ and } R_j = j \cdot r_j \tag{14}$$

where R_j is the radius of j - D sphere circumscribed on j - D simplex, see **Figure 5**.

In particular, for $n=7$, the matrix X (Equation (13)) has 7 columns and 8 rows.

$$X = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.5 & 0.866 & 0 & 0 & 0 & 0 & 0 \\ 0.5 & 0.289 & 0.817 & 0 & 0 & 0 & 0 \\ 0.5 & 0.289 & 0.204 & 0.791 & 0 & 0 & 0 \\ 0.5 & 0.289 & 0.204 & 0.158 & 0.775 & 0 & 0 \\ 0.5 & 0.289 & 0.204 & 0.158 & 0.129 & 0.764 & 0 \\ 0.5 & 0.289 & 0.204 & 0.158 & 0.129 & 0.109 & 0.756 \end{bmatrix} \begin{matrix} A_0 \\ A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \\ A_7 \end{matrix} \tag{15}$$

4. Translation and Reflection of the Simplex

A simplex can be translated and/or rotated in space. Particularly, the simplex defined by X (Equation (13)), with the centre at $A_c = (r_1, \dots, r_n)$, can be parallelly shifted to the centre $P_{c0} = (0, \dots, 0)$ of the co-ordinate system. This way, one obtains a new matrix X_{tr}

$$X_{tr} = \begin{bmatrix} -r_1 & -r_2 & -r_3 & \dots & -r_{n-1} & -r_n \\ R_1 & -r_2 & -r_3 & \dots & -r_{n-1} & -r_n \\ 0 & R_2 & -r_3 & \dots & -r_{n-1} & -r_n \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & R_{n-1} & -r_n \\ 0 & 0 & 0 & \dots & 0 & R_n \end{bmatrix} \tag{16}$$

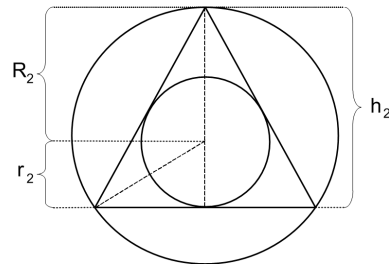


Figure 5. Graphical presentation of r_2 , h_2 and R_2 in 2- D space (Equations (11) and (12)) for $n = 2$.

with R_j and $r_j (j = 1, \dots, n)$ as ones in Equations (11), (12) and (14). Reflection of particular vertices of the matrix X_{tr} in the centre of co-ordinate system $(0, \dots, 0)$ gives the simplex described by the matrix

$$X^* = X_{tr} \cdot (-I) = \begin{bmatrix} r_1 & r_2 & r_3 & \dots & r_{n-1} & r_n \\ -R_1 & r_2 & r_3 & \dots & r_{n-1} & r_n \\ 0 & -R_2 & r_3 & \dots & r_{n-1} & r_n \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & -R_{n-1} & r_n \\ 0 & 0 & 0 & \dots & 0 & -R_n \end{bmatrix} \quad (17)$$

where $I = [\delta_{ij}]$ —identity matrix.

The positions of the simplex presented in Figure 6 (in 2- D space), obtained from (I) by translation (II) and mirror reflection (III) in the origin of ordinate axis, are presented by matrices: X_{tr} and: X^* (Equation (21) for $n = 2$ and

$$X_{tr} = \begin{bmatrix} -r_1 & -r_2 \\ R_1 & -r_2 \\ 0 & R_2 \end{bmatrix} = \begin{bmatrix} -0.5 & -0.289 \\ 0.5 & -0.289 \\ 0 & 0.578 \end{bmatrix}$$

$$X^* = \begin{bmatrix} r_1 & r_2 \\ -R_1 & r_2 \\ 0 & -R_2 \end{bmatrix} = \begin{bmatrix} 0.5 & 0.289 \\ -0.5 & 0.289 \\ 0 & -0.578 \end{bmatrix}$$

Note that the number of k - D walls in n - D simplex equals to the number of $k + 1$ point subsets (k - D walls) generated from the $n + 1$ -point set. From the elementary theory of combinations it results that the number of k - D walls equals to the number of possible combinations of $n + 1$ items taken $k + 1$ at a time, *i.e.*

$$N(n, k) = \binom{n+1}{k+1} = \frac{(n+1)!}{(k+1)!(n-k)!} \quad (18)$$

Particularly, 3- D simplex (tetrahedron, $n = 3$) involves $N(3, 2) = 4$ triangles (2- D walls), $N(3, 1) = 6$ edges (segments, 1- D walls) and $N(3, 0) = 4$ points (vertices, 0- D walls). Generally, the n - D simplex consists of: $N(n, 0) = n + 1$ vertices of the virtual solid stretched on them, $N(n, 1) = n(n + 1)/2$ edges, \dots , $N(n, n - 1) = n + 1$ of $(n - 1)$ - D walls opposite to particular vertices.

5. Simplex Optimization Procedure (SOP)

The simplex method, based on the simplex concept, is considered among the most efficient optimization procedures, successfully applied in different areas of optimization techniques and chemical analyses. The simplex concept is applicable, among others, for optimisation of analytical methods [13], *e.g.* for searching the conditions

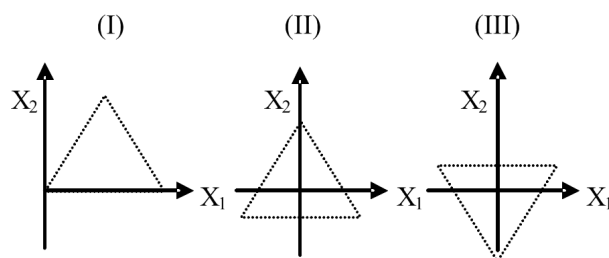


Figure 6. The simplexes obtained after successive (II) translation and (III) reflection of the original simplex (I) in the center of co-ordinate axes in 2-D space; for details—see text.

securing optimal accuracy and precision of an analytical method.

5.1. An Objective Function

The simplex concept is applicable, among others, for optimisation of analytical methods [13]. The variables, x_i (scalars), named as factors forming the vector \mathbf{x} , affect the variable y , named as objective (“target”) function, *i.e.*,

$$y = y(\mathbf{x}) = y(x_1, \dots, x_n) \quad (19)$$

The essence of optimisation is inherent in the objective function. Accuracy and precision are among the most important criteria of analytical methods. Another object functions are related to sensitivity of a method, efficiency of a chemical reaction, etc.

Let us assume that an analytical method aims to find the conditions securing true contents (m_0 , g/g) of an analyte in a sample to be obtained. For this purpose, the following criterion (objective function)

$$y(i) = \frac{1}{N_i} \sum_{k=1}^{N_i} (m_{ik} - m_0)^2 = (\bar{m}_i - m_0)^2 + \left(1 - \frac{1}{N_i}\right) \cdot s_i^2 \quad (20)$$

has been suggested [19], where:

$$\bar{m}_i = \frac{1}{N_i} \cdot \sum_{k=1}^{N_i} m_{ik} \quad (21)$$

$$s_i^2 = \frac{1}{N_i - 1} \cdot \sum_{k=1}^{N_i} (m_{ik} - \bar{m}_i)^2 \quad (22)$$

were calculated in the i -th simplex point, A_i (Equation (3)), on the basis of N_i measurements m_{ik} of an intensive variable m (e.g. number of grams of an analyte contained in a unit mass of solution); m_0 is the true value of this variable, obtained according to a reference method. In the object function (20), both terms, *i.e.* accuracy ($\bar{m} - m_0$) and precision, expressed by standard deviation, $s_i = \sqrt{s_i^2}$, are considered nearly equivalently; the difference in “weights”: 1 and $1 - 1/N_i$, of the two characteristics of the method becomes less significant at higher N_i values.

The function (20) is an example of superposition of different characteristics of a method, *i.e.* accuracy and precision. The optimisation is terminated when the systematic error is insignificant, *i.e.*, the inequality

$$|\bar{m}_i - m_0| < \frac{s_i}{\sqrt{N_i}} \cdot t(0.95, f_i) \quad (23)$$

is fulfilled; $t(0.95, f_i)$ is the critical t -value of the Student’s t -test at $f_i = N_i - 1$ degrees of freedom, on 95% probability level pre-assumed. In particular, for $N_i = 4$, *i.e.* $f_i = 3$, we have $t(0.95, 3) = 3.182$, and then Equation (23) has the form

$$|\bar{m}_i - m_0| < 1.591 \cdot s_i \quad (24)$$

5.2. Decision Variables and Arrangement of Experimental Conditions

The optimization procedure assumes:

1) Selection of natural decision variables, Z_i , as independent (in principle) individual factors affecting the values of the objective function (Equation (19)) and

2) Their order, Z_j ($j = 1, \dots, n$).

The number (n) of the variables Z_j chosen defines the simplex dimension.

The kind (Z_j) and the number (n) of these variables that assume continuous (not discrete) values z_j ($j = 1, \dots, n$), consisting the vector $\mathbf{z} = (z_1, \dots, z_n)^T$, affects the success (efficiency) of optimisation process aiming to get optimal (maximal or minimal) value for the object function, e.g. minimal value for $y = y(i)$ defined by Equation (20). It should be noted that the n -D simplex matrix (Equation (5)) refers—in principle—to orthogonal (independent) variables. The independent variables assuming continuous values are, among others: pH, temperature, time, rate of an operation.

One should be noticed that the form of the matrix (5) enables to add a new variable, Z_{n+1} , to the set of n variables Z_1, \dots, Z_n assumed at the start for optimization—provided that the decision of inclusion of variable Z_{n+1} into the set of variables has been undertaken after measurements done in the points A_0, \dots, A_p , at $p \leq n$, where Z_{n+1} remained unchanged. In this case, the measurements done at the points A_0, \dots, A_p has not to be repeated.

5.3. Design of Experiments and Optimization within the Starting Simplex

The introductory step of the optimization procedure assumes fixing the starting values, z_{0j} , and steps, Δz_j , assumed for Z_j ($j = 1, \dots, n$); these values affect strongly the efficiency of the optimization procedure. Some constraints put on z_j and Δz_j values (resulting from physicochemical, chemical or technological reasons) can also be taken into account. These constraints may result e.g., from limited solubility, possibility of phase change affected by temperature, etc.

The optimization is realized there for values of natural variables calculated from the formula

$$z_{ij} = z_{0j} + x_{ij} \cdot \Delta z_j \quad (25)$$

where $i = 0, 1, \dots, n$ enumerates successive experimental points realized within the initial simplex. The advised values for x_{ij} in (5) are defined in the matrix (13) and specified e.g. in the matrix (15) if $n = 7$. The values $y(j)$, $j = 0, \dots, n$, obtained at $n + 1$ points A_0, A_1, \dots, A_n of the initial simplex are the basis for its further evolution of the simplex.

5.4. Optimization at the Points of Evolving Simplex

At the first stage of the simplex evolution (Figure 7), a point A_{w1} with the worst ($w1$) value, $y(w1)$, for the object function (Equation (20)) is indicated, $w1 \in \{0, n\}$. The point A_{w1} is replaced by a new point, A_{n+1} , obtained by reflection of A_{w1} in the centre, $A_{c1}(\mathbf{x}_{c1})$, of the remaining n points of the initial simplex, i.e., in $n - 1$ -D wall not containing the point A_{w1} . In other words, \mathbf{x}_{c1} is the middle point between \mathbf{x}_{w1} and \mathbf{x}_{n+1} , i.e.,

$$\frac{\mathbf{x}_{w1} + \mathbf{x}_{n+1}}{2} = \mathbf{x}_{c1} = \frac{1}{n} \cdot \sum_{i \neq w1} \mathbf{x}_i \quad (26)$$

After adding the term $(1/n) \cdot \mathbf{x}_{w1}$ to both sides of Equation (26), we obtain the co-ordinates of the new point, A_{n+1} ,

$$\mathbf{x}_{n+1} = \frac{2}{n} \cdot \sum_{i=1}^n \mathbf{x}_i - \left(1 + \frac{2}{n}\right) \cdot \mathbf{x}_{w1} \quad (27)$$

After measurement(s) done at the point A_{n+1} , the values $y(i)$ are compared again within the new (evolved) simplex (containing A_{n+1} and not containing A_{w1}) and the point A_{w2} with the worst value, $y(w2)$ is chosen. Then A_{w2} is reflected in the centre of $n - 1$ -D wall of the new simplex (not containing $w2$). This way, a new point A_{n+2} is obtained and further operations are repeated again, in cyclic manner. At q -th reflection one can write

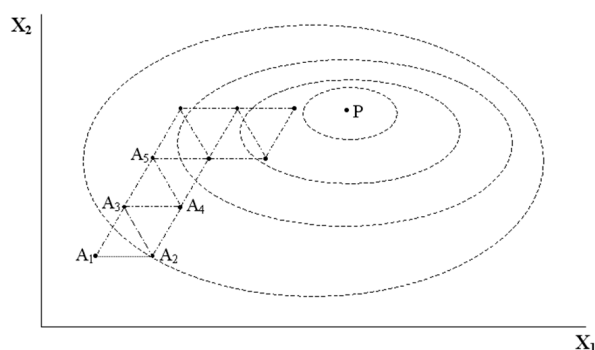


Figure 7. Evolving simplex in 2-D space.

$$\frac{\mathbf{x}_{wq} + \mathbf{x}_{n+q}}{2} = \mathbf{x}_{cq} = \frac{1}{n} \cdot \sum_{i \neq wq}^{(q)} \mathbf{x}_i \quad (28)$$

In the example presented above, the initial (symmetrical) shape of the evolving simplex is maintained owing to the fact that 1) mirror reflections are applied and 2) equal statistical weights are assumed to all the simplex points considered. Sometimes we are forced to move the simplex within a constrained component space [20].

The evolving simplex approaches the *quasi*-optimal region, where $y(i)$ values do not change distinctly. In this region, the evolving simplex should be contracted or diminished (Figure 8); such operations enter e.g. the MINUIT program. The contraction/dilatation and weighting are involved in the relation [21] [22]

$$\mathbf{x}_{n+q} = (1 - \alpha) \cdot \mathbf{x}_{wq} + \alpha \cdot \mathbf{x}_{cq} \quad (29)$$

where the parameter α results from re-parametrization of the a line passing through 2 points: one of them is \mathbf{x}_{wq} , the second one is the centre \mathbf{x}_{cq} of area of q -th, $n-1$ -D simplex, defined as follows

$$\mathbf{x}_{cq} = \frac{\sum_{i \neq wq}^{(q)} p_i \mathbf{x}_i}{\sum_{i \neq wq}^{(q)} p_i} \quad (30)$$

where the operator $\sum_{i \neq wq}^{(q)}$ means summation within q -th $n-1$ -D simplex (\mathbf{x}_{wq} excluded). The contraction or expansion and weighting (“weights” p_i) different points \mathbf{x}_i deforms the evolving simplex gradually. As a rule, it is not an advantageous occurrence during the optimization procedure, however. The simplex deformation is influenced mainly by the weighting factors [23]. Moreover, a shape of response function may sometimes cause the optimum searching impossible, even in 2-D space.

6. Example of SOP

To illustrate the principle of SOP, a simple example of gravimetric analysis is considered below. The matrix expressed by Equation (15) was chosen for initial simplex, and Equation (20) was applied as criterion of optimization. $N_i = 4$ measurements were made at each simplex point. In our case, the relation (24) is chosen as the criterion of optimization. Analyses were made with CdSO_4 solution of ($m_0 = 0.01272 \text{ gCd/1g}$), standardised according to electrogravimetry, considered as the reference method.

6.1. Analytical Prescription

The samples, ca. 5 mL of the solution, weighed on analytical balance ($\pm 0.1 \text{ mg}$), were taken for analysis. The samples were treated with tartaric acid (0.220 g/mL) solution and then with 2.51 mol/L NaOH solution. After dilution with water, the solution was treated with 8-hydroxyquinoline (HL) solution (3.00% m/v, in ethanol) added dropwise from burette, with defined rate of addition. The mixture was leaved for defined time on the water-bath for re-crystallisation of the precipitate CdL_2 at defined temperature, then filtered, washed with water, dried to a constant mass at 105°C and weighed.

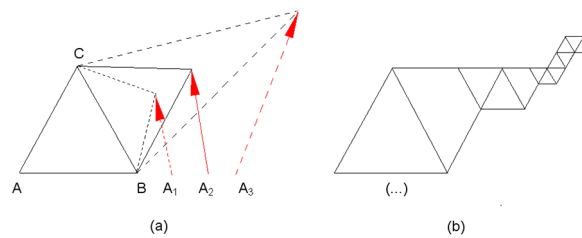


Figure 8. (a) The contraction (A_1), reflection (A_2) i expansion (A_3) of the vertex A of the simplex ABC ($n = 2$) on the edge BC ; and (b) Diminution of the simplex.

6.2. Decision Variables

- Z_1 —re-crystallisation time [min] of the precipitated CdL_2 ;
- Z_2 —mass [g] of tartaric acid added in the solution;
- Z_3 —volume [ml] of NaOH added;
- Z_4 —volume [ml] of 8-hydroxyquinoline added;
- Z_5 —rate [ml/min] of 8-hydroxyquinoline addition;
- Z_6 —temperature [$^{\circ}C$] of water bath where re-crystallization of CdL_2 occurs;
- Z_7 —volume [ml] of the solution before precipitation.

For example, the value $z_{04} = 7.20$ [ml] refers to variable Z_4 ; the related value $\Delta z_4 = 1.00$ ml. For $i = 3$ and $j = 4$, from **Table 1** we have $z_{34} = 8.00 + 0.817 \times 1.00 \cong 8.82$.

6.3. Results of Analyses within the Initial Simplex

The simplex optimisation procedure was realized in experiments performed in all points of the initial simplex (rows $0, \dots, 7$ in **Table 1**). In each point A_i ($i = 0, \dots, 7$), $N_i = 4$ measurements were done. The results m_{ik} [gCD/g] are presented in **Table 2**.

On the basis of the data in **Table 2**, the $y(i)$ values were calculated (last column in **Table 1**).

As results from detailed calculations done on the basis of results in **Table 2**, the inequality (23) has not been fulfilled within the initial simplex and then the evolution of the simplex was needed.

Referring to the **Table 1**, the worst ($w = w_1$) result within the initial simplex was obtained at the point A_2 . During the simplex evolution, this point was reflected in the centre x_{c1} of the remaining points of the starting simplex. Referring to **Table 1**, we have, for example,

$$\begin{aligned} x_{2c1} &= (2 \cdot 0 + 5 \times 0.289) / 7 = 0.206 \\ (0.866 + x_{82}) / 2 &= 0.206 \rightarrow x_{82} = -0.454 \\ z_{82} &= 3.00 + (-0.454) \times 1 \cong 2.55 \\ x_{3c1} &= (2 \times 0 + 0.817 + 4 \times 0.204) / 7 = 0.233 \\ (0 + x_{83}) / 2 &= 0.233 \rightarrow x_{83} = 0.466 \\ z_{83} &= 8.00 + 0.466 \times 1 \cong 8.47 \end{aligned}$$

At the point A_8 , the condition (24) has not been fulfilled as well, and further evolution of the simplex was required. The worst $y(w_2)$ value within the new simplex was stated in the point A_7 . Further calculations referred to the new point A_9 are exemplified below:

$$\begin{aligned} x_{2c2} &= (2 \times 0 + 4 \times 0.289 + 1 \times (-0.454)) / 7 = 0.1004 \\ (0.289 + x_{92}) / 2 &= 0.1004 \rightarrow x_{92} = -0.088, \\ z_{92} &= 3.00 + (-0.088) \times 1 \cong 2.91; \end{aligned}$$

Table 1. The values for z_{ij} assumed in points of the initial (columns 1-7, rows 0-7) and evolving (columns 1-7, rows 8-10) simplexes. For all points, the values $y(i)$ were obtained on the basis of $N_i = 4$ measurements.

$i \blacktriangledown$	$j \blacktriangleright$	$\Delta z_i \blacktriangleright$	1	2	3	4	5	6	7	$y(i) \cdot 10^8$
0	z_{0j}	60	60	3.00	8.00	7.20	1.00	60	100	1.2
1	z_{1j}	120	120	3.00	8.00	7.20	1.00	60	100	0.7
2	z_{2j}	90	90	3.87	8.00	7.20	1.00	60	100	3.0
3	z_{3j}	90	90	3.29	8.82	7.20	1.00	60	100	1.9
4	z_{4j}	90	90	3.29	8.20	7.99	1.00	60	100	0.7
5	z_{5j}	90	90	3.29	8.20	7.36	1.78	60	100	1.3
6	z_{6j}	90	90	3.29	8.20	7.36	1.13	67.5	100	0.8
7	z_{7j}	90	90	3.29	8.20	7.36	1.13	61	138	2.3
8	z_{8j}	90	90	2.55	8.47	7.56	1.30	62.5	111	1.3
9	z_{9j}	90	90	2.91	8.34	7.46	1.21	62	65	1.8
10	$z_{10,j}$	90	90	2.80	7.59	7.69	1.40	63	93	0.5

Table 2. Results of measurements done within the initial simplex.

A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7
0.01260	0.01265	0.01256	0.01256	0.01265	0.01262	0.01262	0.01255
0.01263	0.01268	0.01252	0.01258	0.01267	0.01255	0.01268	0.01259
0.01257	0.01259	0.01249	0.01269	0.01260	0.01267	0.01261	0.01262
0.01268	0.01265	0.01267	0.01255	0.01264	0.01262	0.01264	0.01253

$$x_{3c2} = (2 \times 0 + 0.817 + 3 \times 0.204 + 0.467) / 7 = 0.271$$

$$(0.204 + x_{93}) / 2 = 0.271 \rightarrow x_{93} = 0.338$$

$$z_{93} = 8.00 + 0.338 \times 1 \cong 8.34$$

$$x_{7c2} = (6 \times 0 + 0.216) / 7 = 0.031$$

$$(0.756 + x_{97}) / 2 = 0.031 \rightarrow x_{97} = -0.694,$$

$$z_{97} = 100 + (-0.694) \times 50 \cong 65.$$

The coordinates of the new points: A_8 , A_9 and A_{10} for evolving simplexes, calculated with use of the coded variables x_{ij} specified.

$$\begin{bmatrix} 0.5 & -0.454 & 0.467 & 0.361 & 0.295 & 0.249 & 0.216 \\ 0.5 & -0.088 & 0.338 & 0.261 & 0.214 & 0.180 & -0.694 \\ 0.5 & -0.196 & -0.412 & 0.494 & 0.404 & 0.341 & -0.137 \end{bmatrix} \begin{matrix} A_8 \\ A_9 \\ A_{10} \end{matrix}$$

The optimisation procedure has been terminated at the point A_{10} , where $\bar{m}_i = 0.01267$ and variance $s_i^2 = 0.32 \times 10^{-8}$ were found on the basis of 4 measurements and then the inequality (24)

$$|0.01267 - 0.01272| < 0.56 \times 10^{-4} \times 1.591 = 0.89 \times 10^{-4}$$

was fulfilled and

$$y(10) = (0.01267 - 0.01272)^2 + (1 - 1/4) \times 0.32 \times 10^{-8} = 0.49 \times 10^{-8} \cong 0.5 \times 10^{-8}$$

6.4. Optimal Prescription

On the basis of the optimization procedure, one can formulate the following prescription.

The samples, ca. 5 ml of the standardised CdSO_4 solution, weighed on analytical balance (± 0.1 mg), were

taken for analysis. The solution was treated with 2.80 g of tartaric acid and then with 7.9 ml of 2.5 mol/l NaOH solution. After dilution with water up to ca 90 ml, the solution was treated with 7.7 ml of 3% (m/v) 8-hydroxyquinoline solution (added dropwise from burette, with the rate 1.4 ml/min. The mixture was leaved for ca. 90 min on the water-bath for re-crystallisation of the precipitate CdL_2 at temperature 63°C , then filtered, washed with water, dried to a constant mass at 105°C and weighed.

7. Final Comments

In this paper, the simplex method has been presented in terms known from elementary algebra and geometry. On the basis of scalar product and length of vectors in normalized scale, the co-ordinates of simplex vertices in n - D space were determined. A criterion of optimization, where accuracy and precision of measurements were considered equivalently, has been suggested.

The simplex method was considered as the most efficient among optimization procedures, applicable in simulating procedures realized in recursive computer programs used for simulation purposes and in optimization of analytical procedures. The simplex method requires only one additional experiment, regardless of the number of factors being varied. This drastically reduces the number of experiments required to reach the optimum.

References

- [1] Anderson, V.L. and McLean, R.A. (1974) Design of Experiments: A Realistic Approach. Marcel Dekker, Inc., New York, 363.
- [2] Nelder, J.A. and Mead, R. (1965) A Simplex Method for Function Minimization. *Computer Journal*, **7**, 308-313. <http://dx.doi.org/10.1093/comjnl/7.4.308>
- [3] Walters, F.H., Parker, L.R., Morgan, S.L. and Deming, S.N. (1991) Sequential Simplex Optimization. CRC Press, Boca Raton. <http://www.chem.sc.edu/faculty/morgan/pubs/SequentialSimplexOptimization.pdf>
- [4] Spendley, W., Hext, G.R. and Himsworth, F.R. (1962) Sequential Application of Simplex Designs in Optimisation and Evolutionary Operation. *Technometrics*, **4**, 441-461. <http://dx.doi.org/10.1080/00401706.1962.10490033>
- [5] Fletcher, R. (1965) Function Minimization without Evaluating Derivatives—A Review. *Computer Journal*, **8**, 33-41. <http://dx.doi.org/10.1093/comjnl/8.1.33>
http://folk.uib.no/ssu029/Pdf_file/Fletcher65.pdf
- [6] Olsson, D.M. and Nelson, L.S. (1975) The Nelder-Mead Simplex Procedure for Function Minimization. *Technometrics*, **17**, 45-51. <http://dx.doi.org/10.1080/00401706.1975.10489269>
- [7] Fletcher, R. and Powell, M.J.D. (1963) A Rapidly Convergent Descent Method for Minimization. *Computer Journal*, **6**, 163-168. <http://dx.doi.org/10.1093/comjnl/6.2.163>
- [8] Fletcher, R. and Reeves, C.M. (1964) Function Minimization by Conjugate Gradients. *Computer Journal*, **7**, 149-154. <http://dx.doi.org/10.1093/comjnl/7.2.149>
- [9] Lagarias, J.C., Reeds, J.A., Wright, M.H. and Wright, P.E. (1998) Convergence Properties of the Nelder-Mead Simplex Algorithm in Low Dimensions. *SIAM Journal of Optimization*, **9**, 112-147. <http://dx.doi.org/10.1137/S1052623496303470>
<http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.120.6062&rep=rep1&type=pdf>
- [10] Box, G.E.P. and Hunter, J.S. (1957) Multi-Factor Experimental Designs for Exploring Response Surfaces. *Annals of Mathematical Statistics*, **28**, 195-241. <http://dx.doi.org/10.1214/aoms/1177707047>
- [11] Box, G.E.P. and Draper, N.R. (1969) Evolutionary Operation. John Wiley & Sons, Inc., New York.
- [12] Massart, D.L., Vandeginste, B.G.M., Deming, S.N., Michotte, Y. and Kaufman, L. (1988) Chemometrics: A Textbook. Elsevier, Amsterdam.
- [13] Massart, D.L., Vandeginste, B.G.M., Buydens, L.M.C., De Jong, S., Lewi, P.J. and Smeyers-Verbeke, J. (1997) Handbook of Chemometrics and Qualimetrics. In: *Data Handling in Science and Technology*, Vol. 22, Elsevier, Amsterdam.
- [14] Box, G.E.P. (1957) Evolutionary Operation: A Method for Increasing Industrial Productivity. *Journal of the Royal Statistical Society. Series C (Applied Statistics)*, **6**, 81-101. <http://en.wikipedia.org/wiki/EVOP>
- [15] Hahn, G.J. (1976) Process Improvement Using Evolutionary Operation. 204-206. <http://rube.asq.org/statistics/2011/11/quality-tools/process-improvement-through-simplex-evop.pdf>
- [16] James, F. (2004) MINUIT Tutorial, Function Minimization, Geneva. Reprinted from the Proceedings of the 1972 CERN Computing and Data Processing School, Pertisau, 10-24 September 1972 (CERN 72-21).

<http://seal.web.cern.ch/seal/documents/minuit/mntutorial.pdf>

- [17] Liu, Q. (2001) Implementing Reusable Mathematical Procedures Using C++, C/C++. *Users Journal*.
- [18] Walters, F.H., Parker Jr., L.R., Morgan, S.L. and Deming, S.N. (1991) Sequential Simplex Optimization. CRC Press, Boca Raton.
- [19] Michałowski, T., Rokosz, A. and Wójcik, E. (1980) Optimization of the Conventional Method for Determination of Zinc as 8-Oxyquinolate in Alkaline Tartrate Medium. *Chemia Analityczna*, **25**, 563-566.
- [20] Palasota, J.A., Leonidou, I., Palasota, J.M., Chang, H.-L. and Deming, S.N. (1992) Sequential Simplex Optimization in a Constrained Simplex Mixture Space in Liquid Chromatography. *Analytica Chimica Acta*, **270**, 101-106.
[http://dx.doi.org/10.1016/0003-2670\(92\)80096-P](http://dx.doi.org/10.1016/0003-2670(92)80096-P)
- [21] Deming, S.N. and Morgan, S.L. (1973) Simplex Optimization of Variables in Analytical Chemistry. *Analytical Chemistry*, **45**, 278A-283A.
- [22] Deming, S.N. and Morgan, S.L. (1983) Teaching the Fundamentals of Experimental Design. *Analytica Chimica Acta*, **150**, 183-198. [http://dx.doi.org/10.1016/S0003-2670\(00\)85470-7](http://dx.doi.org/10.1016/S0003-2670(00)85470-7)
- [23] Umeda, T. and Ichikawa, A. (1971) A Modified Complex Method for Optimization. *Industrial & Engineering Chemistry Process Design and Development*, **10**, 229-236.

Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

Other selected journals from SCIRP are listed as below. Submit your manuscript to us via either submit@scirp.org or [Online Submission Portal](#).

