Application of Computer in Chemistry SSC 3533

OPTIMIZATION

Prof. Mohamed Noor Hasan
Dr. Hasmerya Maarof
Department of Chemistry

Introduction

- Optimization is a process of finding a set of conditions that produce the best results.
- In developing a new method or to improve existing methods, we study the effect of certain variables (factors) on the results obtained.
- Example of variables: Temperature, pH, pressure, concentration etc.
- In laboratory experiments, we need to optimize the variables in order to produce better results.
- The term ‘better results’ could mean higher accuracy, better selectivity, faster operation, higher yield, etc.

Examples

- Atomic Absorption Spectroscopy (AAS)

  Factors: level of light, width of slit and monochromator, flame condition, flow rate of fuels and oxidant

- Organic Synthesis

  Factors: temperature, pressure, concentration, concentration of starting materials

- Chromatographic Separation

  Factors: column length, polarity of solvents, pH, temperature etc.

Optimization Problems

- Multidimensional in nature

  Many factors affecting the results of an experiment

- Factors are not independent

  Factors are dependent on one another. When one factor is changed, will affect other factors. Interaction among factors.

Optimization Methods

- **Changing one factor at a time**

  Suitable for experiments in which the variables are independent. Example in GC separation, no relation between flow rate and sample size.

- **Grid Search**

  Evaluate response of various sets of variables that form grid. When a grid area with high response is found, size of the grid can be reduced focusing to area that produce good results only.

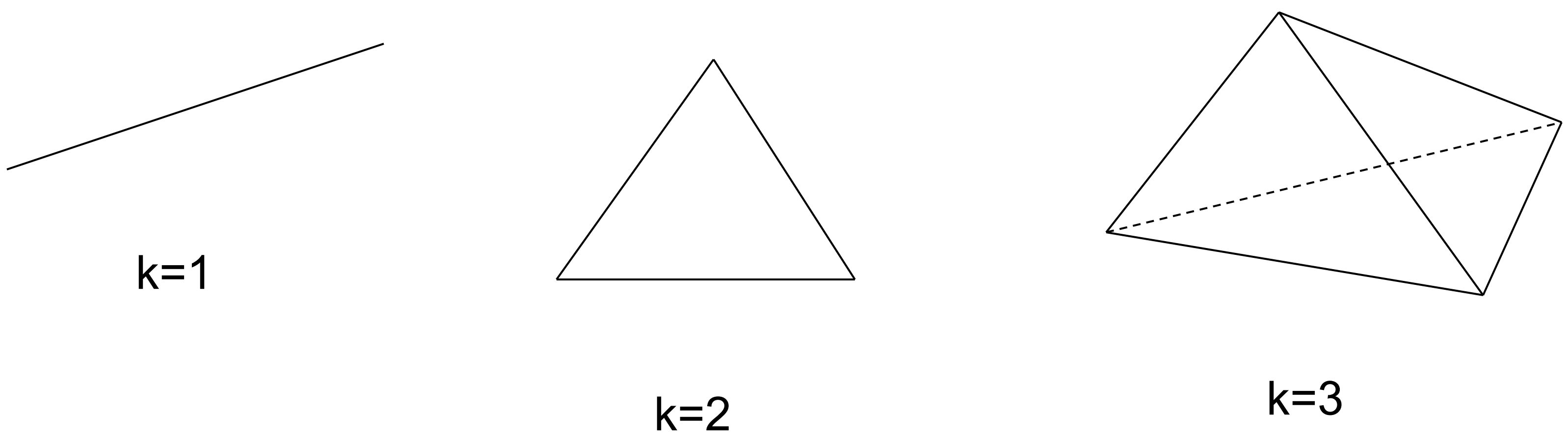
Optimization Methods (Cont.)

- **Random Method** – Use samples that differ in values and selected randomly. This method is not very economical because a lot of time is spent evaluating areas that might not be useful

- **Simplex Method** – Random selection is replace with a more systematic approach based on statistical design. Evaluate response and used it to plan direction towards optimised conditions. First introduce by Spendley et al. (1962) Improved and modified by Nelder and Mead (1965).

Simplex

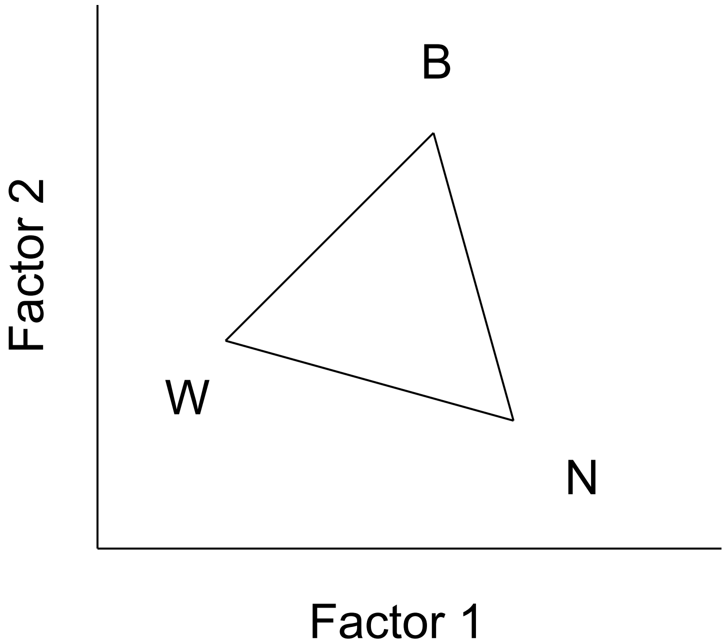
- Simplex is a geometrical shape with number of vertices is one more than the number of dimensions in factor space
- Number of vertices = k+1 , k – no. of factors



Optimization Procedure

- Select quantity (response) to be optimized
  Example: % yield, resolution, sensitivity, selectivity
- Select factors affecting the experiment
  Example: temperature, pH, concentration
- Choose the factor step size
  Should cause a comparable change in response
- Build the first simplex based on the number of factors.
  Eg: If factor = 2 (k=2), the simplex is a triangle (k+1=3).
- Perform the experiment at the 3 initial conditions, measure response and give ranking (B, N, W)
- Label each vertex according to value of response.

Labeling a simplex



B – Best (best response)

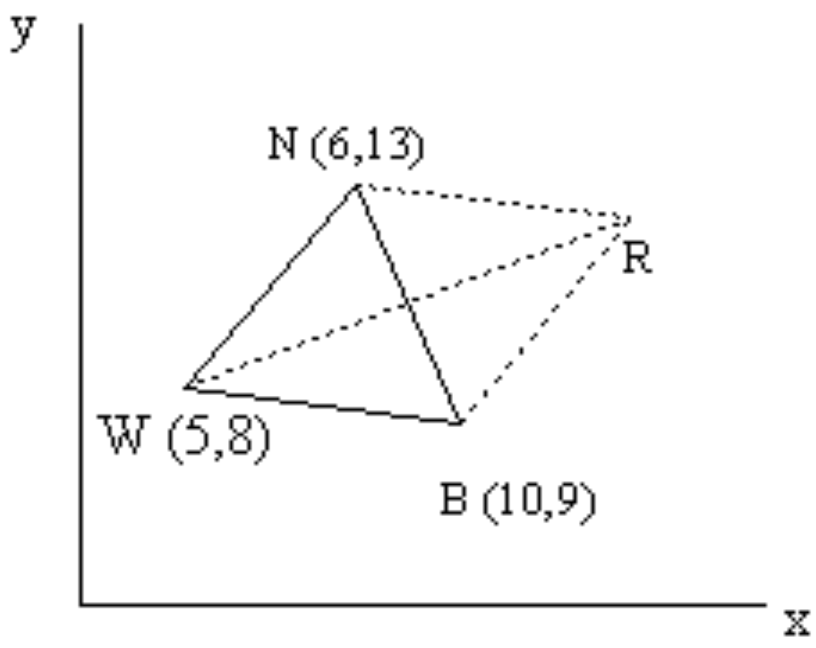
N – Next (next to best)

W – Worst (worst response)

Rules for simplex movement

- **Rule 1**
  Simplex can be moved only by making a new measurement.
- **Rule 2**
  A simplex is moved by discarding the vertex with the least desirable response (*W*) and replacing it with its image (*R*) across the centroid, *C*.
  Example
- **Rule 3**
  If the reflected vertex has the least desirable response in the new simplex, do not reapply Rule 2, but instead reject the second lowest response in the simplex.
- **Rule 4**
  If a vertex has been retained in k + 1 simplexes, re-evaluate the response (repeat the experiment) at the persistent vertex. This is to prevent error in measurement causing the oscillation.
- **Rule 5**
  If a new vertex lies outside the boundaries of factors, do not make an experimental observation, instead, assign to it a very undesirable response (eg. a negative response) to force the simplex back inside the boundaries.

Example calculation of new vertex



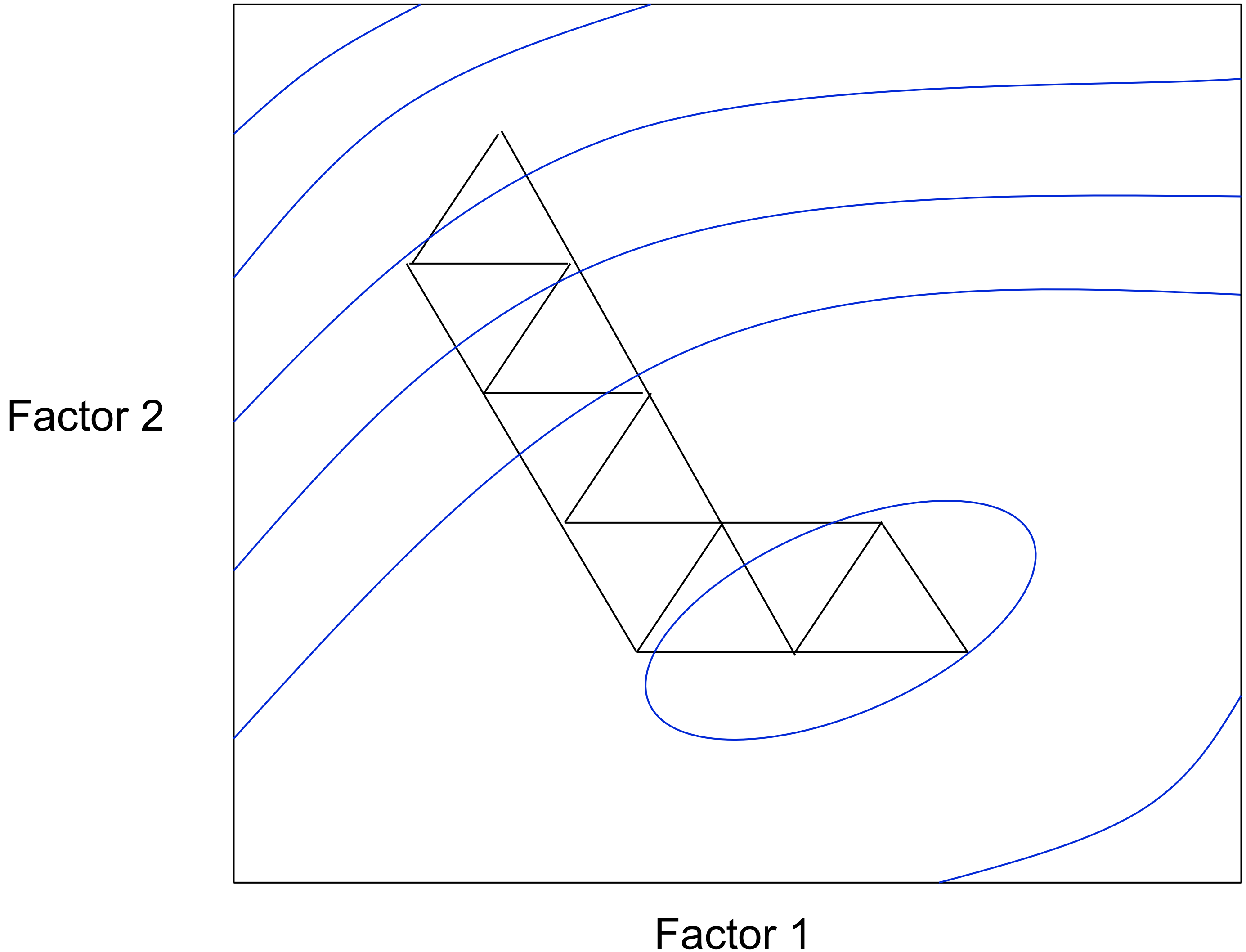
$R = C + (C - W)$

$C = ½ (N + B)$

$C = ½ (x_1 + x_2 , y_1 + y_2)$
$= ½ (6 + 10 , 13 + 9)$
$= (8, 11)$

$R = (8,11) + [(8,11) - (5,8)]$
$= (8,11) + (3,3)$
$= (11,14)$

Simplex Movement



Determination of step size

	Factor No.				
Vertex No.	1	2	3	4	5
1	0	0	0	0	0
2	1.00	0	0	0	0
3	0.500	0.866	0	0	0
4	0.500	0.289	0.817	0	0
5	0.500	0.289	0.204	0.791	0

Determination of first simplex (2 factors)

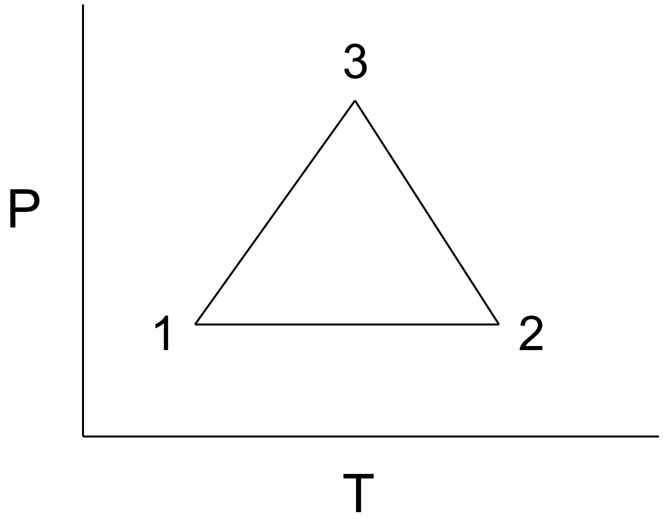
- An experiment is influenced by two factors, temperature and pressure.
- Initial conditions:
  Factor 1: Temperature = 25 ^{o}C
  Factor 2: Pressure = 70 mm Hg
- Step size for factor 1 = 10 $_{o}$C (SST)
  Step size for factor 2 = 10 mm Hg (SSP)

UTM

Example of first simplex

Vertex	Temp (^oC)	Pressure (mm Hg)
1	25	70
2	25 + (SST x 1) = 35	70 + (SSP x 0) = 70
3	25 + (SST x 0.50) = 30	70 + (SSP x 0.86) = 78.66

First Simplex



1 = (25, 70)
2 = (35, 70)
3 = (30, 78.66)

Exercise

Two factors, temperature and pH, influence the level of impurities in the product of a synthesis. The goal of the optimization is to seek values of temperature and pH that produce the lowest level of impurities.

In theory, the level of impurities is related with those factors according to formula:

$$Y = 2 + a^2 - 2a + 2b^2 - 3b + (a - 2)(b - 3)$$

Y – % impurities

a – temperature

b - pH

Exercise (Cont.)

Temperature	pH
0	0
1	0
0.5	0.866

By using the above values of pH and temp. as initial conditions, perform the simplex optimization to obtain set of temperature and ph that produce the lowest level of impurities.

Problems with the fixed-size simplex

- It is not always clear when an optimum has been reached
- There is no way to accelerate the optimization process
- Achievement of optimized condition is very much dependent on original size of the simplex
- Problems with the optimization if random errors or noise are high

Modified simplex method

- Simplex size can be modified, make it larger or smaller, in order to reach the optimum condition faster.
- Also called Variable-size Simplex method
- First introduced by Nelder dan Mead (1965)

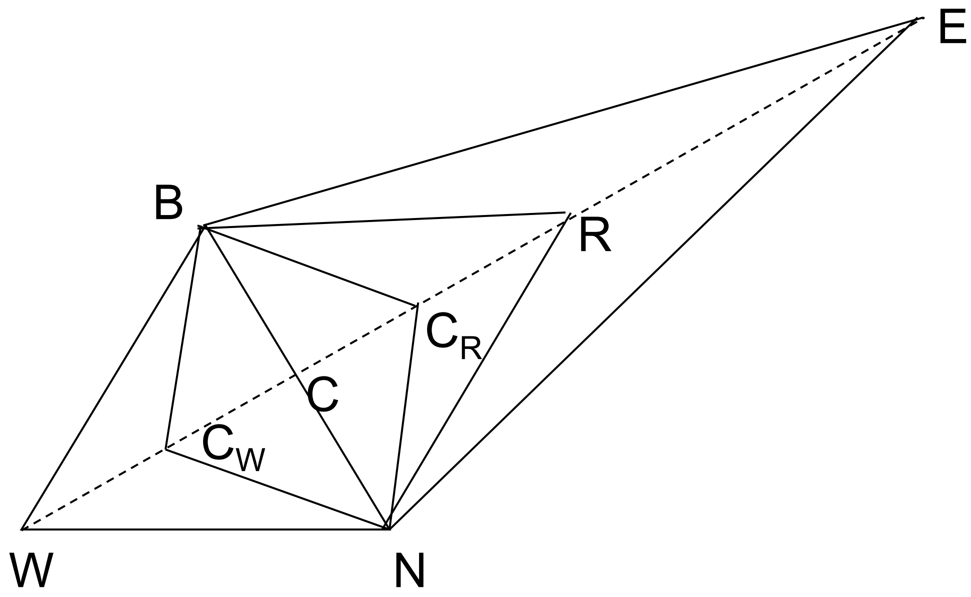
  J.A. Nelder and R. Mead "A Simplex method for function minimisation", *Computer Journal,* **7**(1965), 308-313

Rules of modified simplex method

- If the response at R is better than at B, extend to E with CE = 2CR
  E = R + (R - C)
- If the response at E < B no need for expansion.
- If the response at R is between B and N no need for expansion and contraction. Maintain the original size of simplex.
- If response at R < N, we are heading towards the wrong direction. The simplex should be contracted.
- a) If response at R < N but R > W: C_R between C and R
  $C_R = C + (C-W)/2$

  b) If R < W: C_W between R and W
  $C_W = C - (C-W)/2$

Variable-size simplex



Examples of Applications

- Optimization of Gas Chromatography
- Optimization of HPLC