

Simplex Optimization of Chemical Systems

Simplex optimization (1, 2) has been shown to be an efficient developmental technique for the improvement of response in chemical methods (3-20). However, application of this technique to methods development has been carried out only at the level of graduate research. Optimization experiments, modified or simplified for use by undergraduate students, are virtually nonexistent. Therefore, a laboratory experiment was designed which would demonstrate the use of simplex optimization in a simple and straightforward manner.

Optimization is important in many areas of chemistry. In analytical chemistry, for example, improving absorbance response for a fixed amount of determinant (21) often leads to a desirable increase in both sensitivity and precision. Synthetic organic and inorganic chemistry as well as chemical engineering all benefit from an increase in reaction yield, especially if the overall yield results from a series of stepwise reactions: the final yield is then the algebraic product of all intermediate yields (18).

Hazards of single-factor-at-a-time optimization strategies have been discussed previously (10). The inefficiencies of sequential factorial designs are also well known (9). The sequential simplex method of optimization (1, 2) is a strategy that rapidly and efficiently locates the region of the optimum by varying all factors (variables) simultaneously. The rules of the simplex algorithm are presented here for completeness. More detailed discussions may be found in the literature (1-4, 6, 9, 10).

Simplex Rules

The variable size simplex method of Nelder and Mead (2) is a logical algorithm consisting of reflection, expansion, and contraction rules. These rules can be understood by referring to the two-dimensional example shown in Figure 1. The algorithm can be used with any number of dimensions.

A simplex is a geometric figure defined by a number of points ($n + 1$) equal to one more than the number of variables (dimensions). In the initial simplex **BNW** shown in Figure 1, Vertex **B** was measured and found to have the best response, **W** the worst response, and **N** the next-to-the-worst response. **P** is the centroid of the face remaining when the worst vertex is eliminated (6).

Reflection is accomplished by extending the line segment **WP** beyond **P** to generate the new vertex **R** (i.e., a new set of experimental conditions)

$$R = \bar{P} + (\bar{P} - W) \quad (1)$$

Three possibilities exist for the measured response at **R**.

1) The response at **R** is more desirable than the response at **B**. An attempted expansion is indicated and the new vertex **E** is generated:

$$E = \bar{P} + 2(\bar{P} - W) \quad (2)$$

If the response at **E** is better than the response at **B**, **E** is retained and the new simplex is **NBE**. If the response at **E** is not better than at **B**, the expansion is said to have failed and **BNR** is taken as the new simplex. The algorithm is restarted using the new simplex.

2) If the response at **R** is between that of **B** and **N**, neither ex-

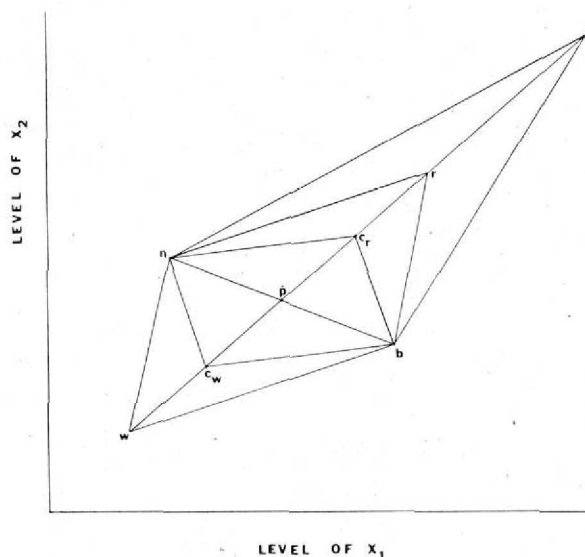


Figure 1. Possible moves in a modified simplex method.

pansion nor contraction is recommended and the process is restarted with the new simplex **BNR**.

3) If the response at **R** is less desirable than the response at **N**, a step in the wrong direction has been made and the simplex should be contracted. One of two possible vertices must be generated:

a) If the response at **R** is worse than the response at **N** but not worse than that at **W**, the new vertex should lie closer to **R** than to **W**:

$$C_r = \bar{P} + 0.5(\bar{P} - W) \quad (3)$$

The process is restarted with the new simplex **BNC_r**.

b) If the response at **R** is worse than the response at **W**, then the new vertex should lie closer to **W** than to **R**:

$$C_w = \bar{P} - 0.5(\bar{P} - W) \quad (4)$$

The process is restarted with the new simplex **BNC_w**.

False high results caused by experimental error which might mislead the simplex can be detected and corrected if the response of a vertex appearing in $n + 1$ successive simplexes is reevaluated (1). The average response can be taken as the response of reevaluated vertices.

If a vertex lies outside the boundaries of one or more of the factors (variables), a very undesirable response is assigned to that vertex. The simplex will then be forced back inside the boundaries.

Calculations are simplified if a worksheet such as the one shown in Figure 2 is used (22).

Experimental

A simple method for introducing the application of simplex optimization to chemical systems is a modification of a vanadium spot test (23). The procedure involves the addition of varying amounts (number of drops) of hydrogen peroxide solution and sulfuric acid solution to a standard amount (number of drops) of a sample of fixed vanadium concentration. After a sufficient time has elapsed, absorbance is measured on a spectrophotometer. The measured absorbance depends upon the amounts of both reagents and exhibits an optimum in each: too little reagent and the reaction is slow or incomplete; too much

¹ University of Houston, Houston, Texas 77004

Vertex No.	X1	X2	X3	X4	X5	X6	Response	Risk	Times Retained
Coordinates of simplex vertices								W	
								N	
Σ									
$\vec{P} = \Sigma / n$									
$\vec{P} - \vec{W}$									
$\frac{1}{n} (\vec{P} - \vec{W})$									
$\vec{R} = \vec{P} + (\vec{P} - \vec{W})$								Vertex no. _____	
$\vec{C}_R = \vec{P} + \frac{1}{2} (\vec{P} - \vec{W})$								Vertex no. _____	
$\vec{C}_W = \vec{P} - \frac{1}{2} (\vec{P} - \vec{W})$								Vertex no. _____	
$\vec{L} = \vec{R} + (\vec{P} - \vec{W})$								Vertex no. _____	

Figure 2. Example of a worksheet which could be used with this experiment.

reagent and the fixed amount of chromophore is diluted or is converted to a less absorbing species (23). The goal of the optimization is to find the amounts of hydrogen peroxide solution and sulfuric acid solution that produce maximum absorbance.

Each student should be provided approximately 250 ml of solution containing about 0.1 g vanadium sulfate (~400 ppm), 250 ml of 20% sulfuric acid solution (v/v), and 250 ml of 1% hydrogen peroxide solution (v/v).

The boundaries for the hydrogen peroxide and sulfuric acid solutions are set at 0 and 100 drops. A standard amount of vanadium solution (20 drops) is placed in a spectrophotometer cell (test tube if a Spectronic 20 is used). Hydrogen peroxide and *then* sulfuric acid (the order of reagent addition is important) are added in amounts dictated by the simplex algorithm and stirring is initiated. Absorbance is measured 5 min after the addition of sulfuric acid. Suggested starting vertices are (10 drops H_2O_2 , 10 drops H_2SO_4), (50, 10), (10, 50).

The following initial number of drops per solution A and solution B were used and categorized according to their responses during experimentation.

	x_1	x_2	
	Drops Solution	Drops Solution	
Vertex	A	B	Relative Response
1	25	33	51.9 worst
2	10	10	62.3 next to worst
3	1	22	67.5 best

In order to start simplex calculations the following steps must be taken:

STEP

- 1 Place the number of drops used per response in the order listed on the worksheet (i.e., worst, next to worst, best responses), as shown in the sample worksheet.
- 2 Take the summation of the next to the worst response and the best response.
3. To obtain \bar{P} divide through the summation by n , where $n = 2$.
- 4 Subtract your worst response from \bar{P} .
- 5 To generate the new vertex R (i.e., a new set of experimental conditions), the following equation must be applied:

$$R = \bar{P} + (\bar{P} - W)$$

where R is the first reflection in the simplex.

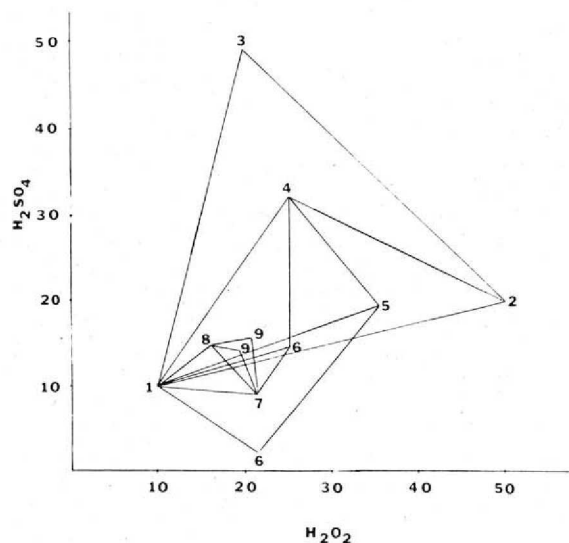
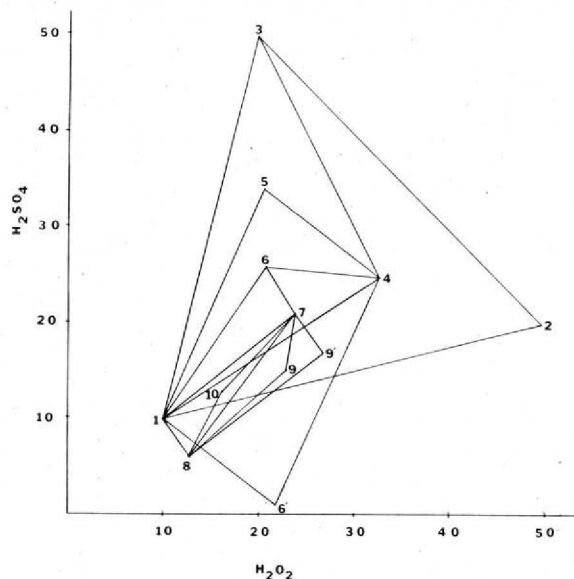


Figure 3. Typical simplex plots of H_2O_2 versus drops of H_2SO_4 .

- 6 If this response at R is more desirable than the response at B (best response), an expansion may be attempted.

The new vertex E is generated by applying the following equation:

$$E = \bar{P} + 2(\bar{P} - W)$$

if the response at E is better than the response at B , E is retained and the new simplex is BNE . If the response at E is not better than at B , the expansion is said to have failed and BNR is taken as the new simplex.

The algorithm is restarted using the new simplex.

However if the response at R is less desirable than at N , we can assume that a step in the wrong direction has been made and the simplex should be contracted. One of two possible vertices must be generated:

- a) If the response at **R** is worse than the response at **N** but not worse than that at **W**, the new vertex should lie closer to **R** than to **W**:

$$C_R = \bar{P} + 0.5(\bar{P} - W)$$

the process is restarted with the new simplex BNC_R .

- b) If the response at \mathbf{R} is worse than the response at \mathbf{W} , then the new vertex should lie closer to \mathbf{W} than to \mathbf{R} :

$$C_W = \bar{P} - 0.5(\bar{P} - W)$$

the process is restarted with the new simplex BNC_w .

In our case, however, we see that the C_W contraction has failed (i.e., giving a negative number of drops), therefore the process is restarted with the new simplex BNC_R , applying the rules previously stated.

Results

Figures 3a and b show the progress of the simplex toward the optimum in a typical laboratory study. The numbers indicate the absorbance response at each vertex. The large initial simplex is seen to contract into a smaller region about the optimum.

As can be seen by these figures, each experiment will predict a slightly different optimum and may take a few more or less simplex steps. However, the student should get a feeling for optimization and approach the same general optimum region.

Literature Cited

- (1) Spendley, W., Hext, G. R., and Himsworth, F. R., *Technometrics*, **4**, 441 (1962).
- (2) Nelder, J. A., and Mead, R., *Computer J.*, **7**, 308 (1965).
- (3) Ernst, R. R., *Rev. Sci. Instrum.*, **39**, 988 (1968).
- (4) Long, D. E., *Anal. Chim. Acta*, **46**, 193 (1969).
- (5) Houle, M. J., Long, D. E., and Smette, D., *Anal. Lett.*, **3**, 401 (1970).
- (6) Deming, S. N., and Morgan, S. L., *Anal. Chem.*, **45**, 278A (1973).
- (7) Czech, F. P., *J. Ass. Offic. Anal. Chem.*, **56**, 1489 (1973).
- (8) Czech, F. P., *J. Ass. Offic. Anal. Chem.*, **56**, 1496 (1973).
- (9) Deming, S. N., and King, P. G., *Res./Develop.*, **25**, 22 (1974).
- (10) Morgan, S. L., and Deming, S. N., *Anal. Chem.*, **46**, 1170 (1974).
- (11) King, P. G., and Deming, S. N., *Anal. Chem.*, **46**, 1476 (1974).
- (12) King, P. G., and Deming, S. N., *Abstracts American Association Clinical Chemists 26th National Meeting, Las Vegas, Nevada, August 1974*, Paper No. 194; *Clin. Chem.*, **20**, 891 (1974).
- (13) King, P. G., *Ph.D. Dissertation*, Emory University, Atlanta, Georgia, 1974.
- (14) Krause, R. D., and Lott, J. A., *Clin. Chem.*, **20**, 775 (1974).
- (15) Smits, R., Vanroelen, C., and Massart, D. L., *Z. Anal. Chem.*, **278**, 1 (1975).
- (16) King, P. G., Deming, S. N., and Morgan, S., *Anal. Lett.*, **8**, 369 (1975).
- (17) Parker, Jr., L. R., Morgan, S. L., and Deming, S. N., *Appl. Spectrosc.*, **29**, 429 (1975).
- (18) Dean, W. K., Heald, K. J., and Deming, S. N., *Science*, **189**, 805 (1975).
- (19) Vickers, T. J., Johnson, E. R., and Wolfe, T. C., *Abstracts Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1975*, Paper No. 136.
- (20) Denton, M. B., and Routh, M. W., *Abstracts Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1975*, Paper No. 391.
- (21) Wilson, A. L., *Talanta*, **17**, 21 (1970).
- (22) Lowe, C. W., *Trans. Inst. Chem. Eng.*, **42**, T334 (1964).
- (23) Feigl, F., and Anger, V., "Spot Tests in Inorganic Analysis," 6th ed., (Translator: Oesper, R. E.), Elsevier, New York, 1972.