

SOP4chem – simplex optimization procedure for chemistry

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Simplex optimization of chemical systems

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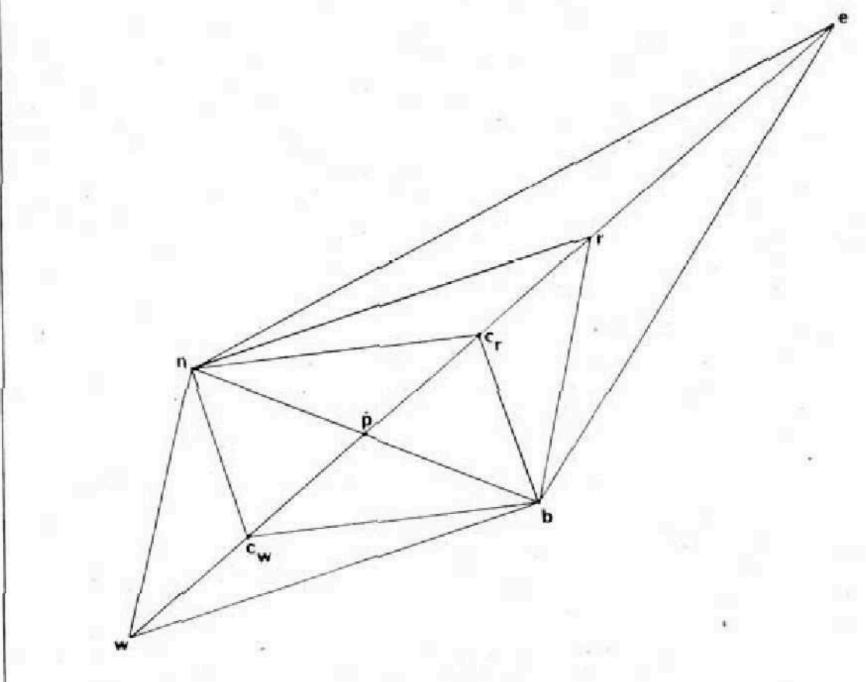
LEVEL OF x_1

Figure 1. Possible moves in a modified simplex method.

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. \bar{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-

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 BNR .

- 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 BNR .

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

These rules are implemented. Additionally, if boundary constraints are employed and a pivot vertex is outside the allowable range, rule 3a is applied repeatedly until pivot vertex is valid.

Input files

- CSV file with initial experiments and ‘scores’/utility values
- First column must be labeled ‘iteration’
- Followed by 2 or more columns with experimental parameters and arbitrary labels
- Last column must be labeled ‘score’

```
iteration,KeV,center,width,score
1.0,40.0,50.0,380.0,4.2
2.0,50.0,100.0,250.0,3.4
3.0,60.0,290.0,570.0,1.3
4.0,70.0,150.0,350.0,2.1
26.02.23.csv (END)
```

Additional number of rows should be one greater than number of experimental variables to properly define simplex. If there are additional rows, extra rows at the top will be ignored.

Input files

- All experimental parameters can be optionally constrained using a second CSV file
- First column must be labeled ‘bound’ and rows must be labeled ‘U’ and ‘L’ for upper and lower bounds.
- Experimental parameters must be in same order as data input CSV.

```
<U+FEFF>bound,KeV,center,width  
U,100.,999999.,999999.  
L,30.,0.,0.  
bounds.csv (END)
```

Unicode encoding character at start of file can be safely ignored. Partial constraints are not supported. Use large magnitude numbers to simulate one-sided bounds.

```
[bash-3.2$ python SOP4chem.py --help  
usage: SOP4chem.py [OPTION] [FILE]
```

Generate next experimental parameters via simplex optimization procedure. CSV file is updated each time. Note: iterations will become sorted due to simplex progression. <https://pubs.acs.org/doi/10.1021/ed056p307>

positional arguments:

file CSV file containing history of experimental parameters.
Format of column labels should be: iteration, 2 or more experimental parameter labels, score.

optional arguments:

-h, --help show this help message and exit
-v, --version show program's version number and exit
-bounds BOUNDS Optional CSV file with bounds for experimental parameters.
Format of column labels should be: bound, same experimental parameter labels as ordered in data CSV file. Row labels should be: U, L for upper and lower bounds respectively.
Defaults to NoneType.

```
bash-3.2$ █
```

```
[bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
    bound      KeV     center      width
0       U   100.0  999999.0  999999.0
1       L    30.0      0.0      0.0
    iteration      KeV     center      width      score
2            3.0    60.0    290.0    570.0      1.3
3            4.0    70.0    150.0    350.0      2.1
1            2.0    50.0    100.0    250.0      3.4
0            1.0    40.0      50.0    380.0      4.2
4            5.0    50.0      5.0    205.0 -99999.0
Please perform the experiment in the latest iteration above.
Then re-run this program and enter new score.
```

```
bash-3.2$
```

```
[bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
```

	bound	KeV	center	width	
0	U	100.0	999999.0	999999.0	
1	L	30.0	0.0	0.0	
	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.3
1	4.0	70.0	150.0	350.0	2.1
2	2.0	50.0	100.0	250.0	3.4
3	1.0	40.0	50.0	380.0	4.2
4	5.0	50.0	5.0	205.0	-99999.0

If you have performed last experiment in table above, please enter new positive score (negative value will exit program): 3.555555

	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.300000
1	4.0	70.0	150.0	350.0	2.100000
2	2.0	50.0	100.0	250.0	3.400000
4	5.0	50.0	5.0	205.0	3.555555
3	1.0	40.0	50.0	380.0	4.200000
5	6.0	35.0	2.5	242.5	-99999.000000

Please perform the experiment in the latest iteration above.

Then re-run this program and enter new score.

```
bash-3.2$ █
```

```
bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
```

	bound	KeV	center	width
0	U	100.0	999999.0	999999.0
1	L	30.0	0.0	0.0

	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.300000
1	4.0	70.0	150.0	350.0	2.100000
2	2.0	50.0	100.0	250.0	3.400000
3	5.0	50.0	5.0	205.0	3.555555
4	1.0	40.0	50.0	380.0	4.200000
5	6.0	35.0	2.5	242.5	-99999.000000

If you have performed last experiment in table above, please enter new positive score (negative value will exit program): 4.3

	iteration	KeV	center	width	score
0	3.0	60.000	290.0000	570.0000	1.300000
1	4.0	70.000	150.0000	350.0000	2.100000
2	2.0	50.000	100.0000	250.0000	3.400000
3	5.0	50.000	5.0000	205.0000	3.555555
4	1.0	40.000	50.0000	380.0000	4.200000
5	6.0	35.000	2.5000	242.5000	4.300000
6	7.0	40.625	9.0625	279.0625	-99999.000000

Please perform the experiment in the latest iteration above.
Then re-run this program and enter new score.

```
bash-3.2$
```

Notes

- The iteration dataframe table stores this simplex values that were used in calculations.
- In some cases, the experimental parameters that you used in additional experiments will be changes according to the simplex rules.
- It should be easy to a create separate log file that records all experimental results if truly needed. Contact the author.