

The Simplex Method and Fuzzy Set Membership Functions to Optimize Analytical Methods

Method Approach and a Case Study From Gas Chromatography

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Background

- Optimization is a common activity in analytical chemistry.
- The simplex method is perhaps the most widely used approach.
- Multiple optimization criterias have been handled using "objective functions".

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Contents

- Characteristics of problems to solve
- Our idea of the solution
- A calculation tool
- A practical case
- Conclusions

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Characteristics of optimization problems to solve

- Several optimization objectives to consider.
- Several control variables of importance.
- Interactivity is beneficial.

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Our idea of the solution

- The simplex method to optimize.
- Response variables described as fuzzy sets.
- An easy-to-use calculation tool that allows for maximum users interaction and all types changes "along the way".

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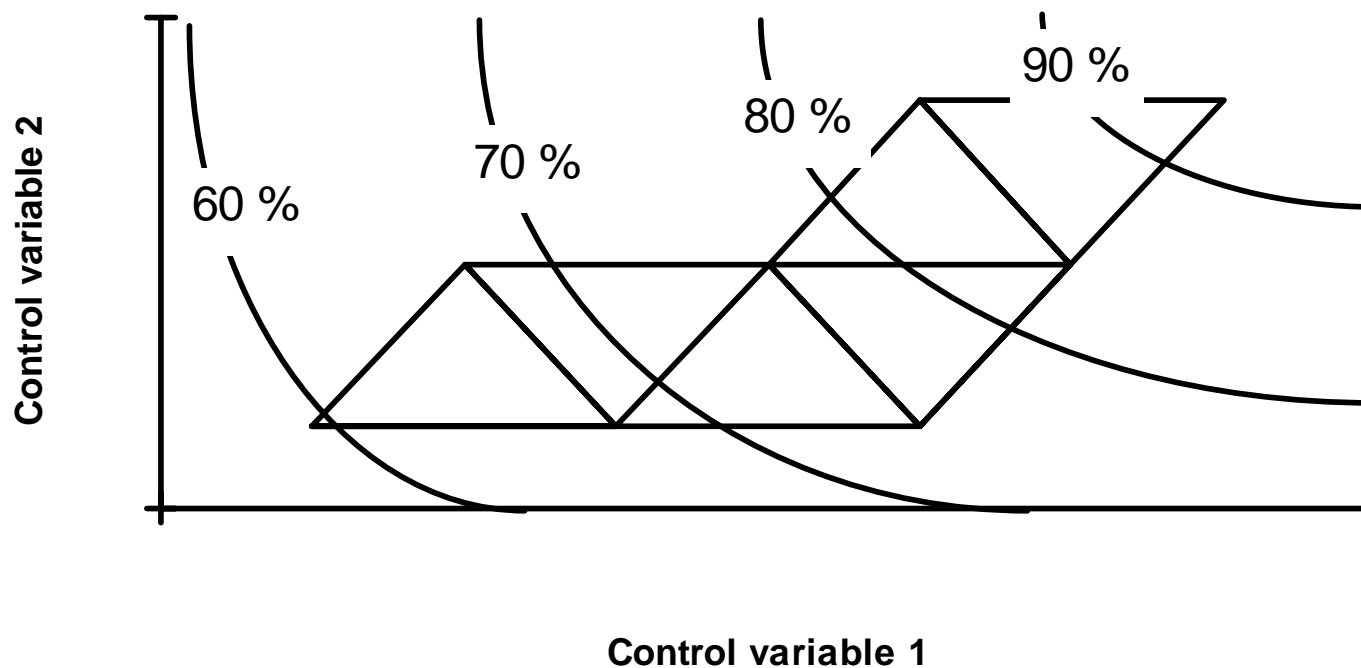
The simplex method

- Easy to understand and apply.
- Initial $k+1$ trials, a "simplex".
- Subsequent trials in the direction of improvement.
- Method characteristics:
 - Sequential.
 - No assumption about an underlying model.
 - Cost-effective, few trials compared with RSM.

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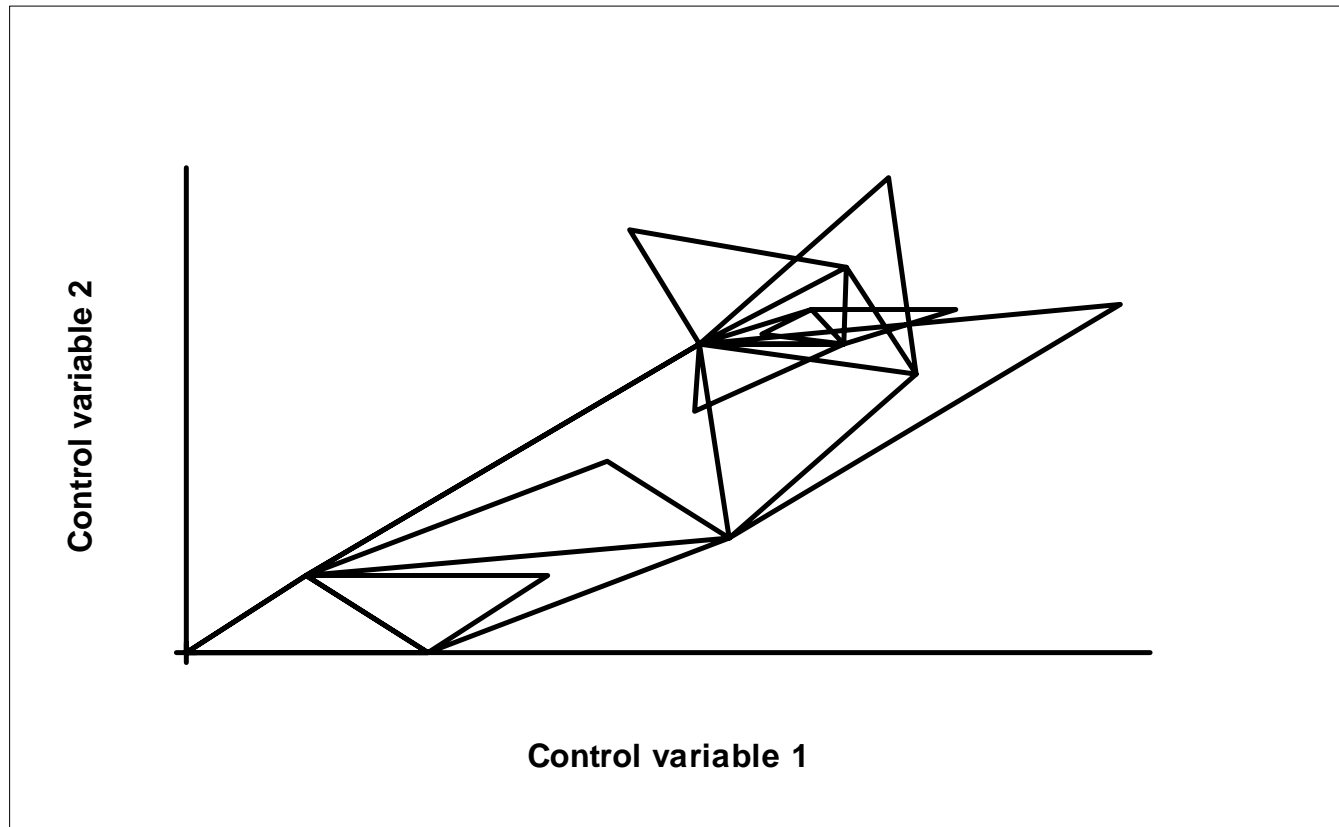
The basic simplex method



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The modified simplex method



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Objective functions

- "An objective function is a mathematical relationship expressing the objective in terms of system factors and/or responses."
- Examples: The ratio separation/analysis time or separation combined with a penalty function for analysis time.
- Fuzzy set membership functions ("desirability functions") is another approach.

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The response variables

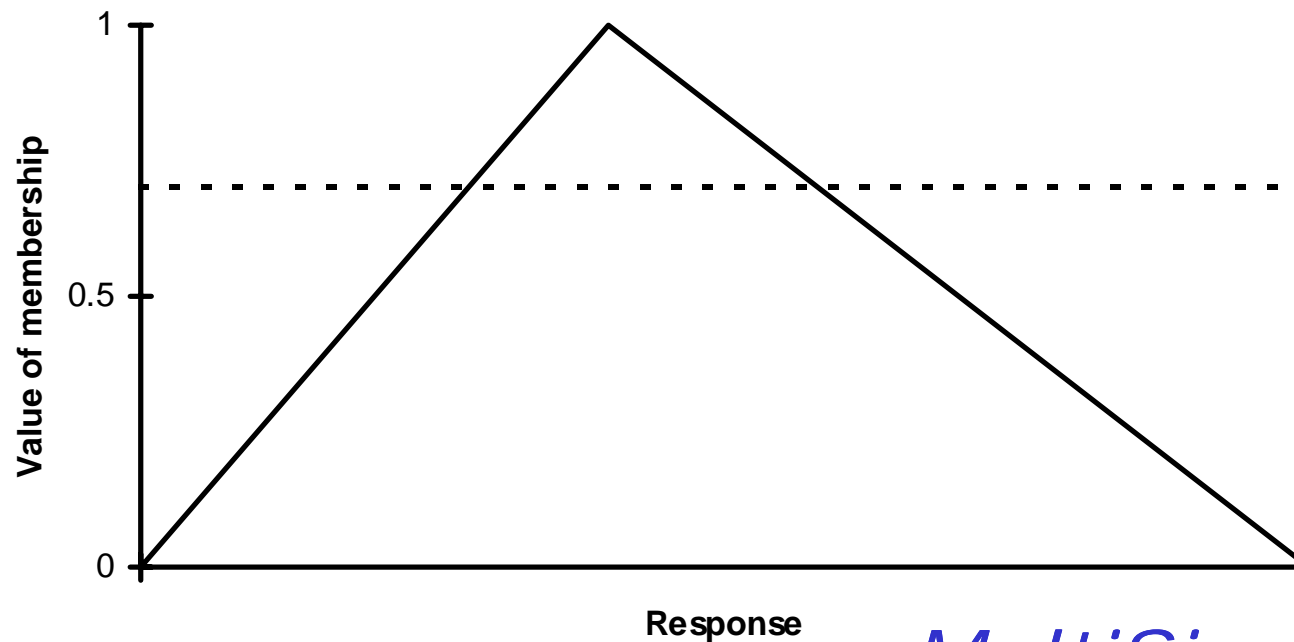
- The response variables are measured with different scales.
- The relative significance of different variables differ.
- For some response variables the objective is maximization, but for others it is minimization or a specific target.

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A membership function

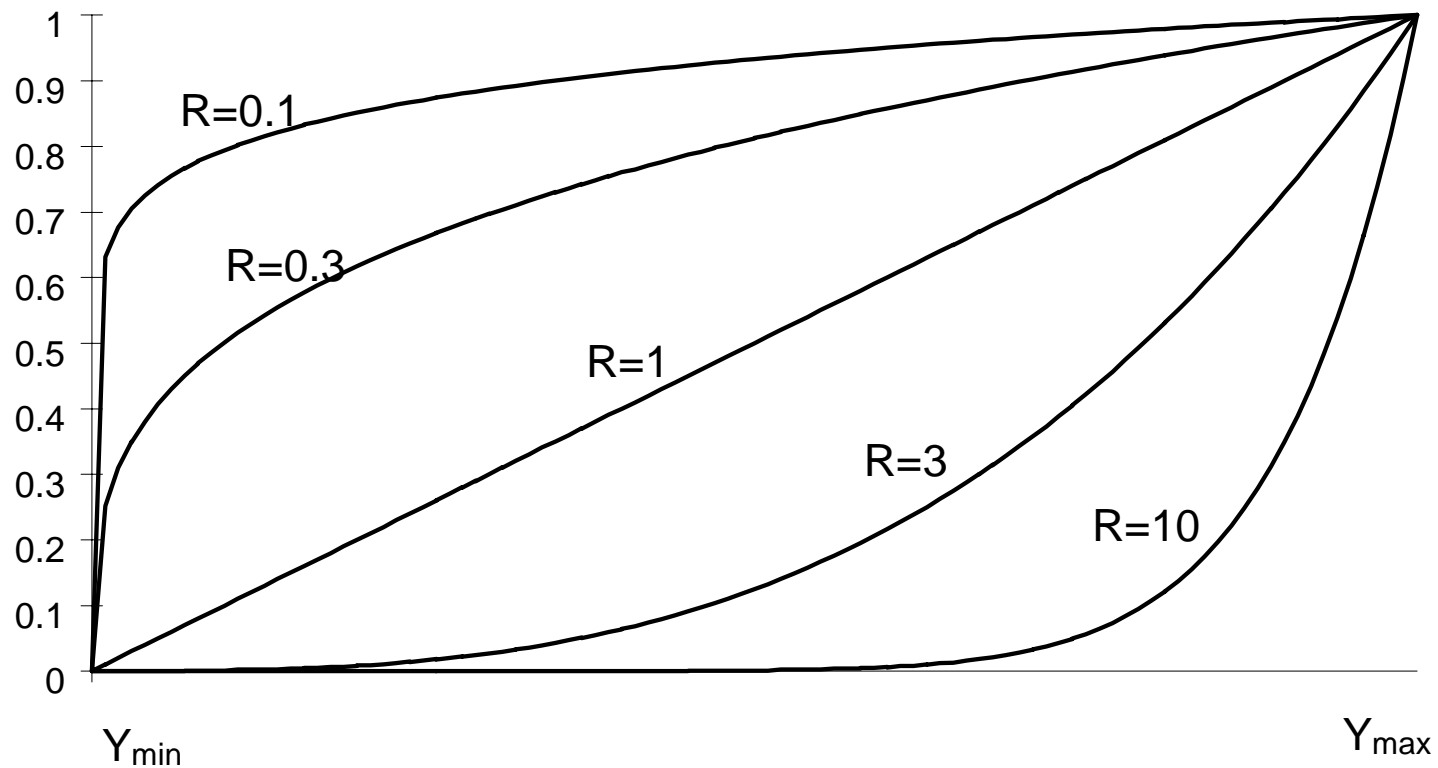
- The objective, i.e. target, is represented by a characteristic function varying between 0 and 1.



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Different shapes



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The aggregated membership

$$M(y) = \frac{\sum_{i=1}^I \beta_i \cdot m(y_i)}{\sum_{i=1}^I \beta_i}, \text{ if all } m(y_i) > 0$$

$$M(y) = 0, \text{ if any } m(y_i) = 0$$

- $M(y)$ = the aggregated value of membership.
- $m(y_i)$ = the membership value for the individual response variable.
- β_i = the influence value for the individual response variable.
- I = the number of response variables.

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A new calculation tool: The MultiSimplex™

- Simplex and fuzzy set calculations as described.
- The user in charge of everything.
- Automatic degeneration check.
- Easy to use and Microsoft® Office Compatible.

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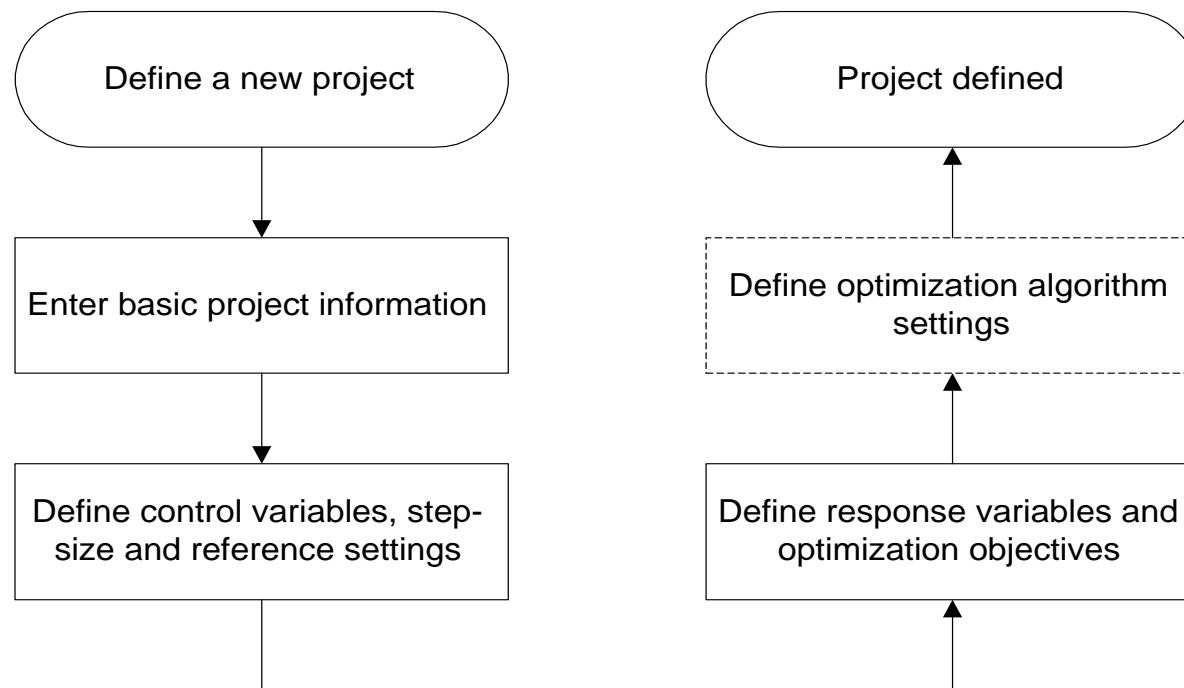
Capabilities

- Up to 15 control variables, and up to 15 response variables.
- Adjustable algorithm settings.
- Efficient D-optimal starting designs.
- Maximization, minimization and target objectives described by adjustable membership functions.

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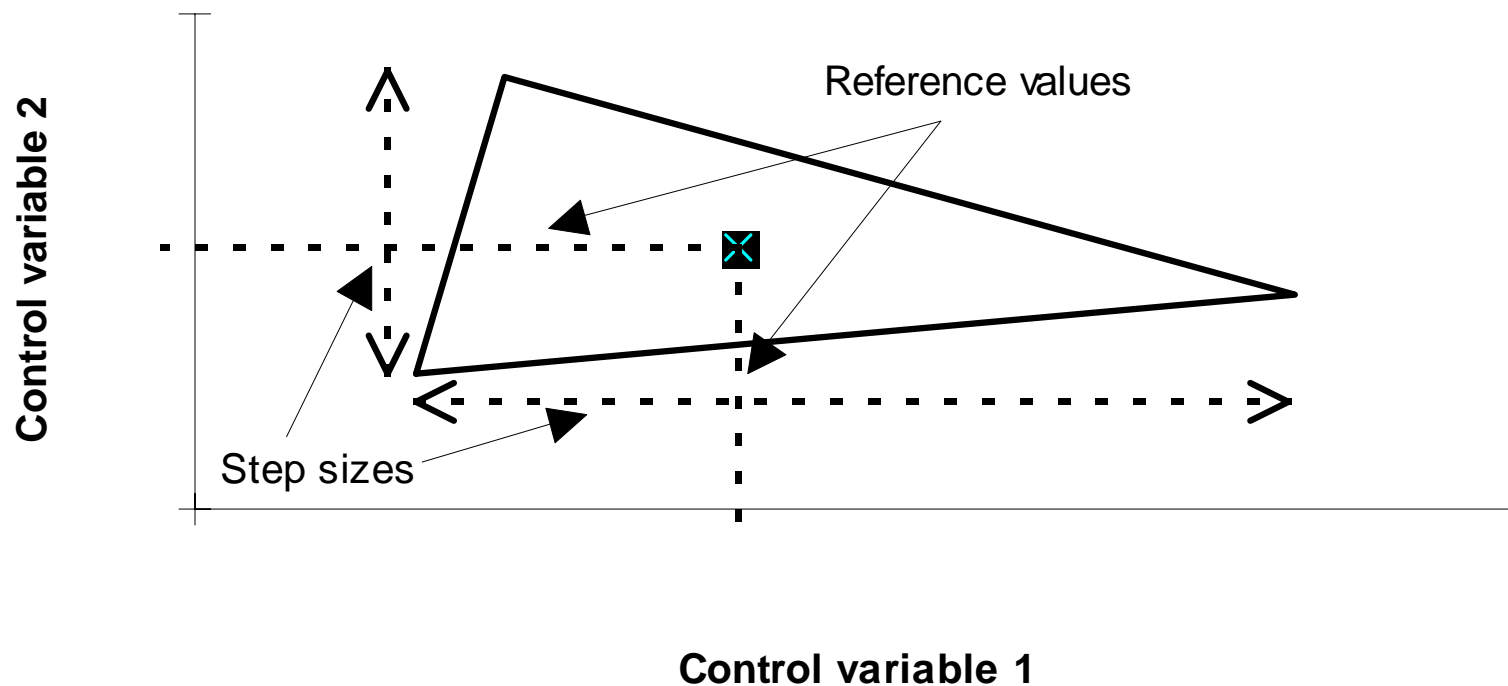
The definition sequence



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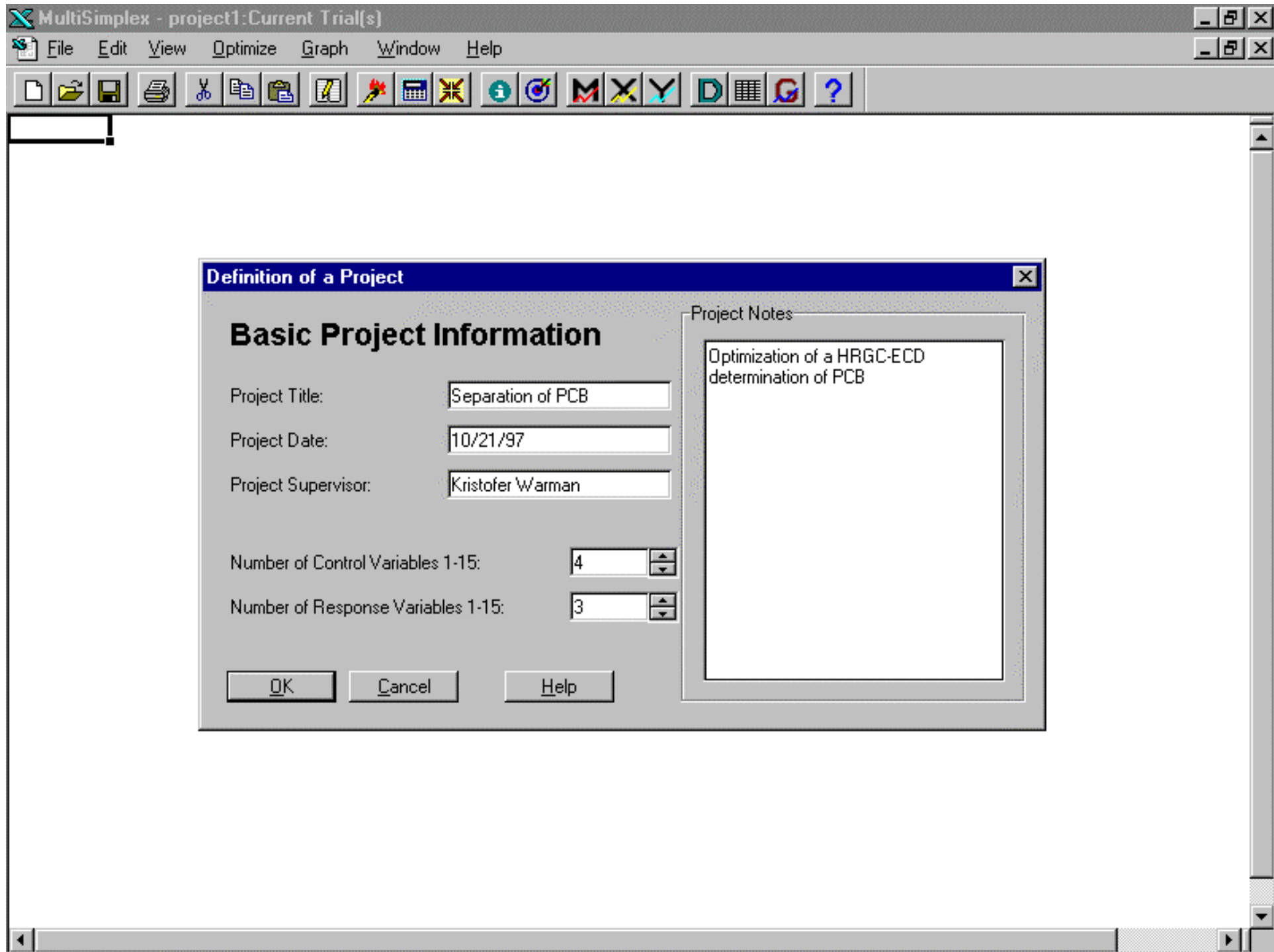
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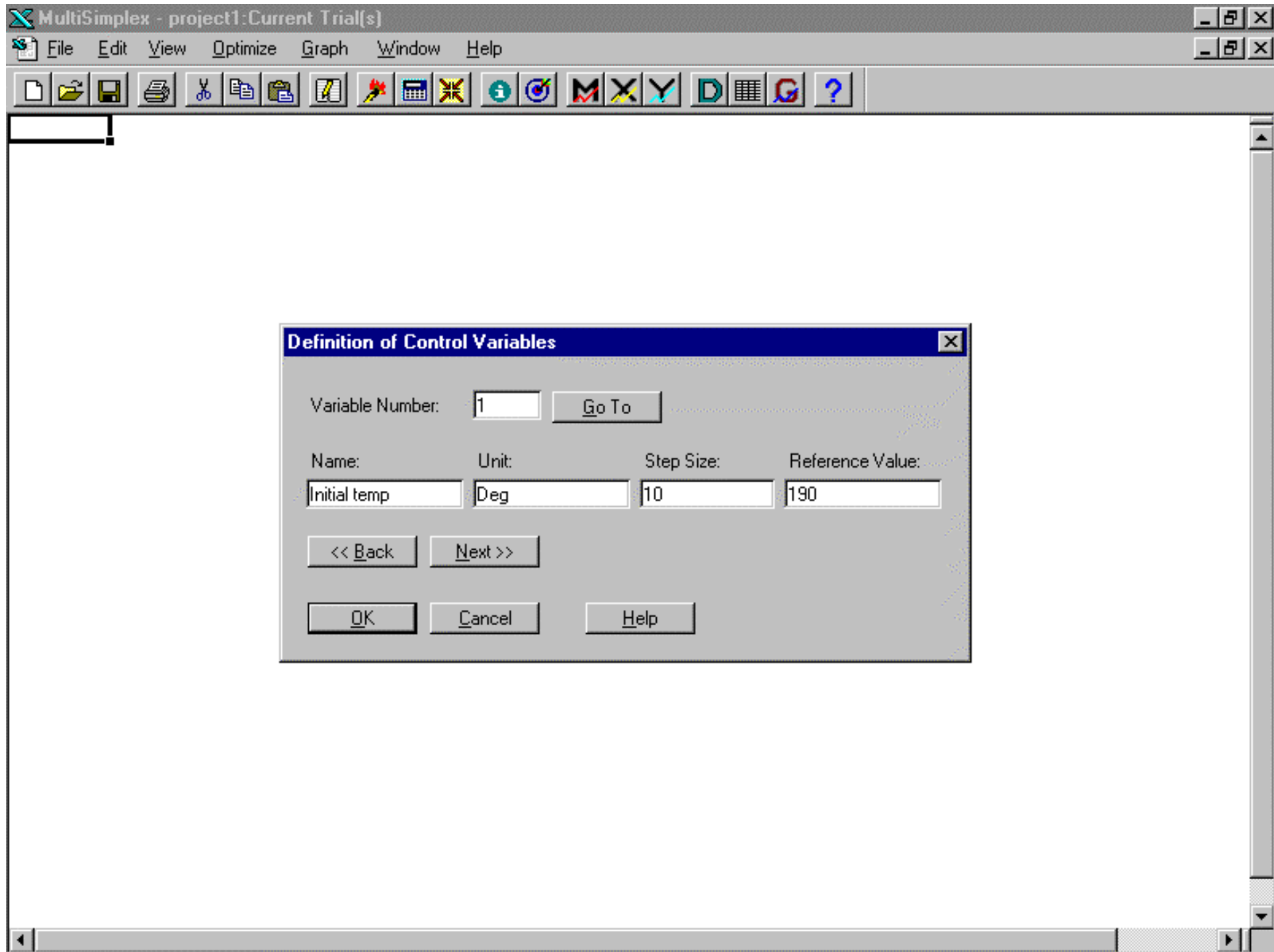
Step size and ref. value

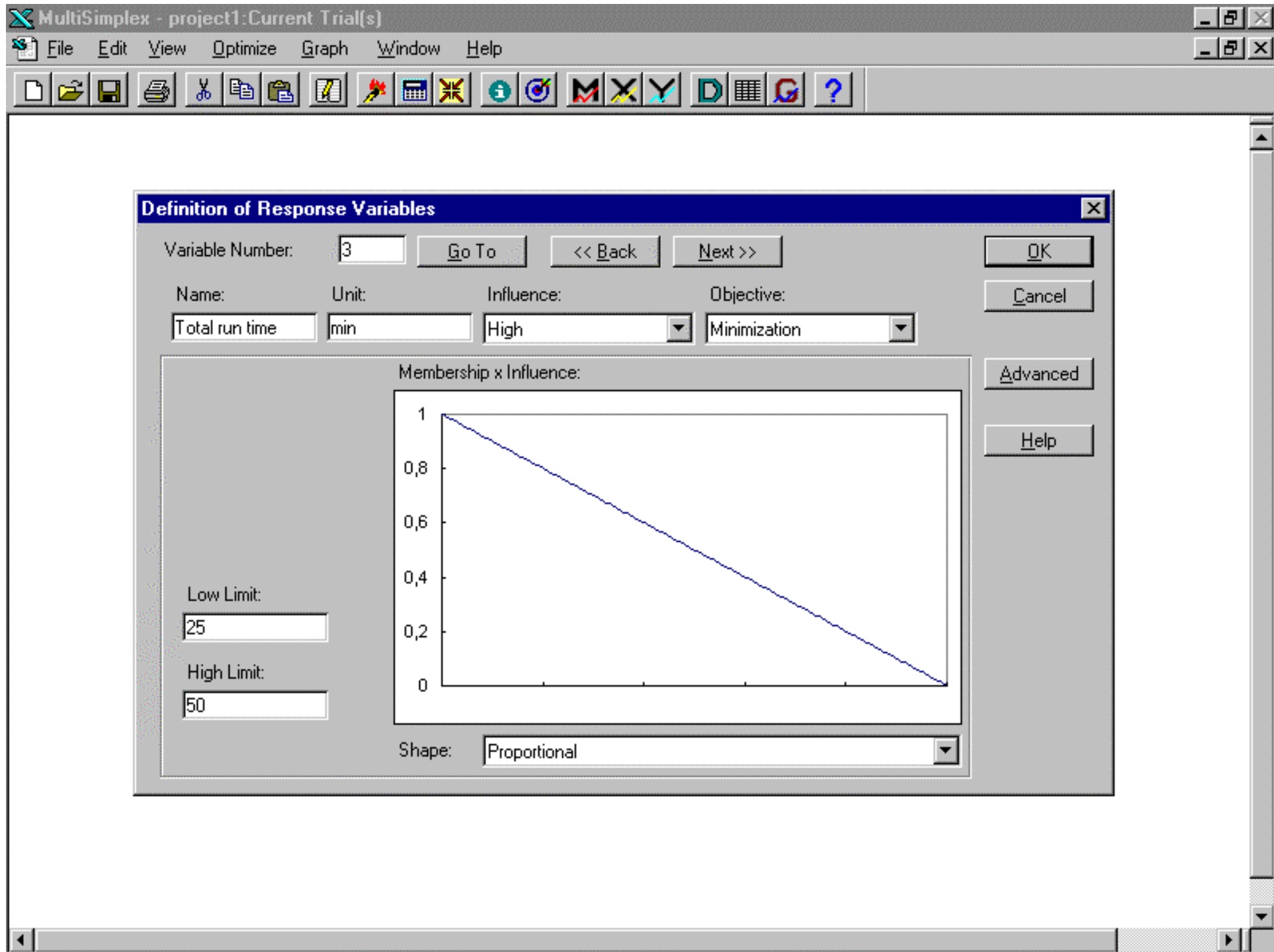


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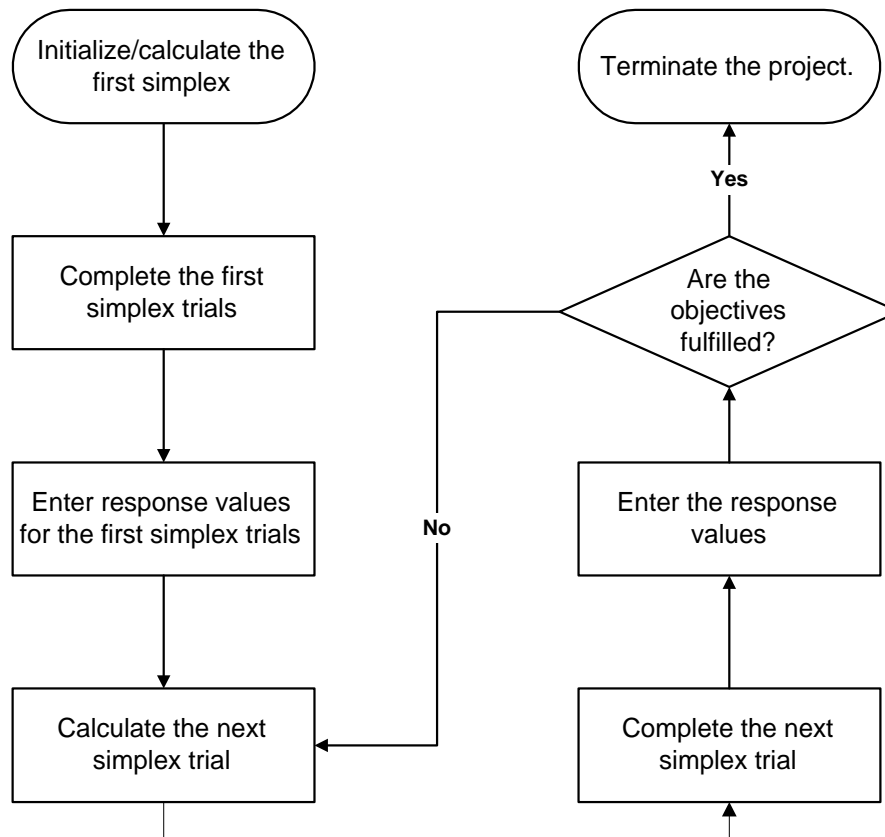
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The optimization sequence



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File Edit View Optimize Graph Window Help

project1:Database

Use	Trial No	Initial temp Deg	Initial time min	Temp gradient Deg/min	Max temp Deg	Resolution #1 R	Resolution #2 R	Total run time min	Used Memb
	1	185	5,0	5,0	295	1,201	1,959	45,063	
	2	195	5,0	7,0	295	1,119	1,811	39,161	
*	3	195	5,0	5,0	305	1,226	2,02	39,69	
*	4	185	3,0	7,0	305	1,135	1,87	34,823	
*	5	195	3,0	5,0	295	1,182	1,992	41,1	
	6	200	3,0	7,0	305	1,115	1,82	32,733	
*	7	208	2,0	8,0	310	1,043	1,725	28,009	
*	8	197	1,5	5,5	313	1,125	1,88	32,683	
	9	198	2,8	7,8	322	1,08	1,735	27,786	
	10	199	2,8	8,1	325	1,016	1,699	24,192	

User's Guide and Reference MultiSimplex

Arkiv Redigera Bokmärke Alternativ Hjälp

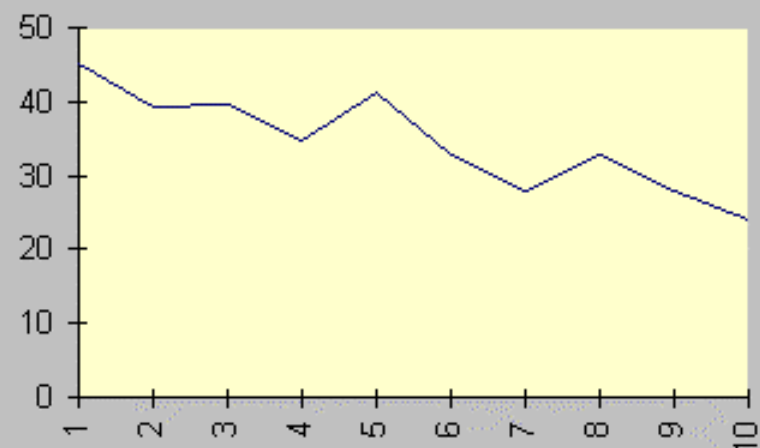
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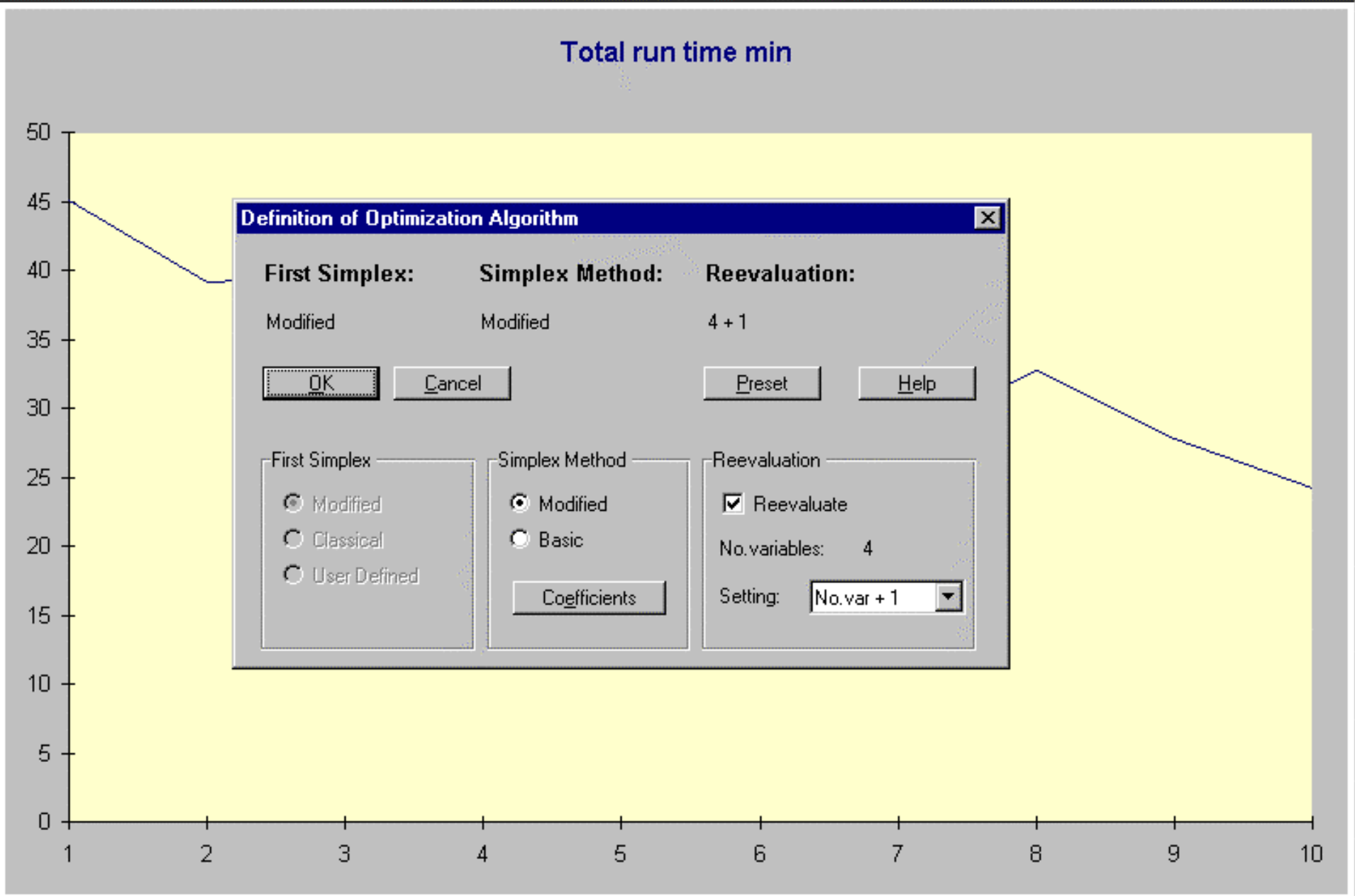
Is there any industrial experience with these methods?

Yes, the methods used in MultiSimplex™ are well established with decades of industrial experience behind. Many scientific and technical papers have also been published on this experience.

project1:Graph

Total run time min





A case study from gas chromatography

- PCB determined by HRGC/ECD.
- Important to keep the total run time short, without jeopardising necessary chromatographic resolution.
- A simplex optimization of the separation conditions is a straightforward solution to this common problem.

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Experimental

- Tests with Aroclor 1248, with PCB #209 as internal standard.
- 3 μ l, 10 ng PCB/ μ l, injected in split mode.
- Capillary: 30 m J&W DB5, 1.0 μ m film, 320 μ m i.d.
- Chromatograph: HP 5890, Series II with autoinjector HP 7673.
- Detector: ECD.

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Control variable settings

	Ref. value	Step size
Initial temperature °C	190	10
Initial time min	4	2
Temperature gradient °C/min	6	2
Maximum oven temp. °C	300	10

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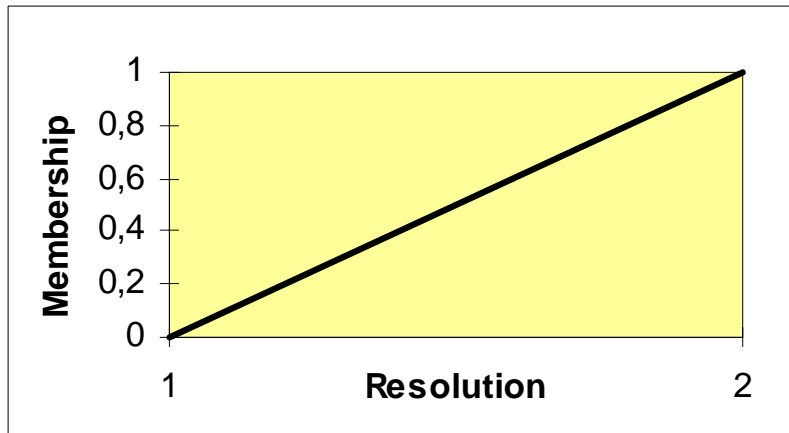
Response variables

- Chromatographic resolution R1, between two peaks in the beginning of the chromatogram. [$R = \frac{X_A - X_B}{0.5(W_A + W_B)}$]
- Chromatographic resolution R2, between two peaks in the late part of the chromatogram.
- Total run time.

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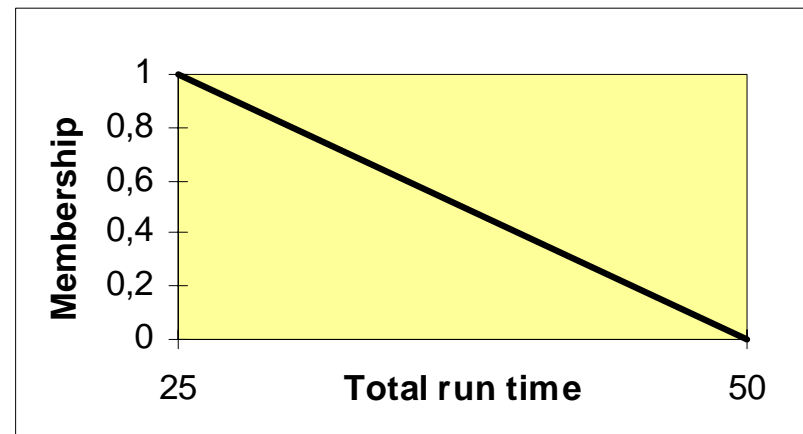
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Membership functions



Influence = 1

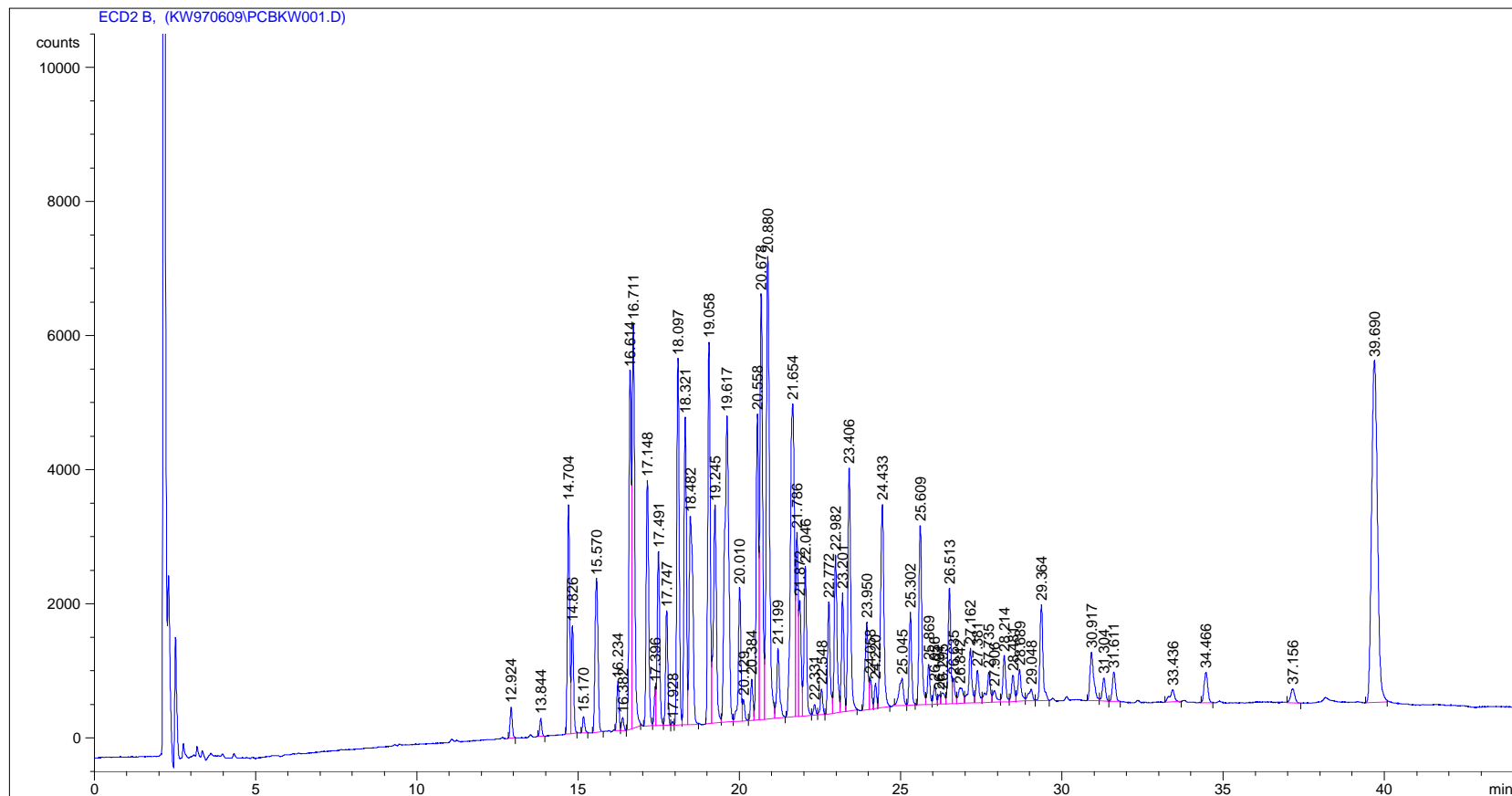
Influence = 0.67



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Chromatogram 1



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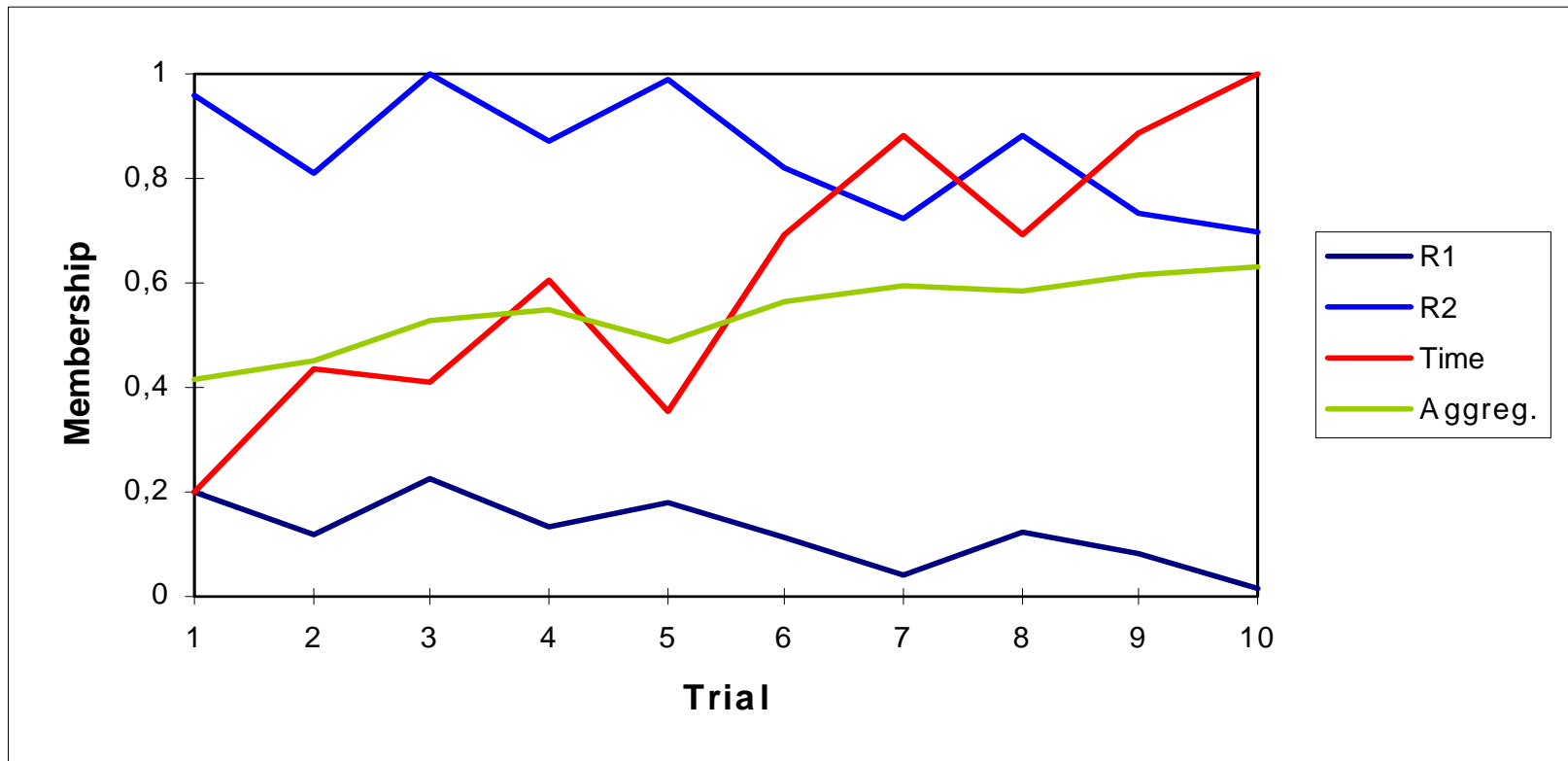
10 trials

Trial No	Initial temp Deg	Initial time min	Temp gradient Deg/min	Max temp Deg	Resolution #1 R	Resolution #2 R	Total run time min	Used Membership
1	185	5,0	5,0	295	1,201	1,959	45,063	0,417
2	195	5,0	7,0	295	1,119	1,811	39,161	0,452
3	195	5,0	5,0	305	1,226	2,02	39,69	0,527
4	185	3,0	7,0	305	1,135	1,87	34,823	0,547
5	195	3,0	5,0	295	1,182	1,992	41,1	0,488
6	200	3,0	7,0	305	1,115	1,82	32,733	0,563
7	208	2,0	8,0	310	1,043	1,725	28,009	0,596
8	197	1,5	5,5	313	1,125	1,88	32,683	0,584
9	198	2,8	7,8	322	1,08	1,735	27,786	0,613
10	199	2,6	9,1	335	1,016	1,698	24,183	0,632

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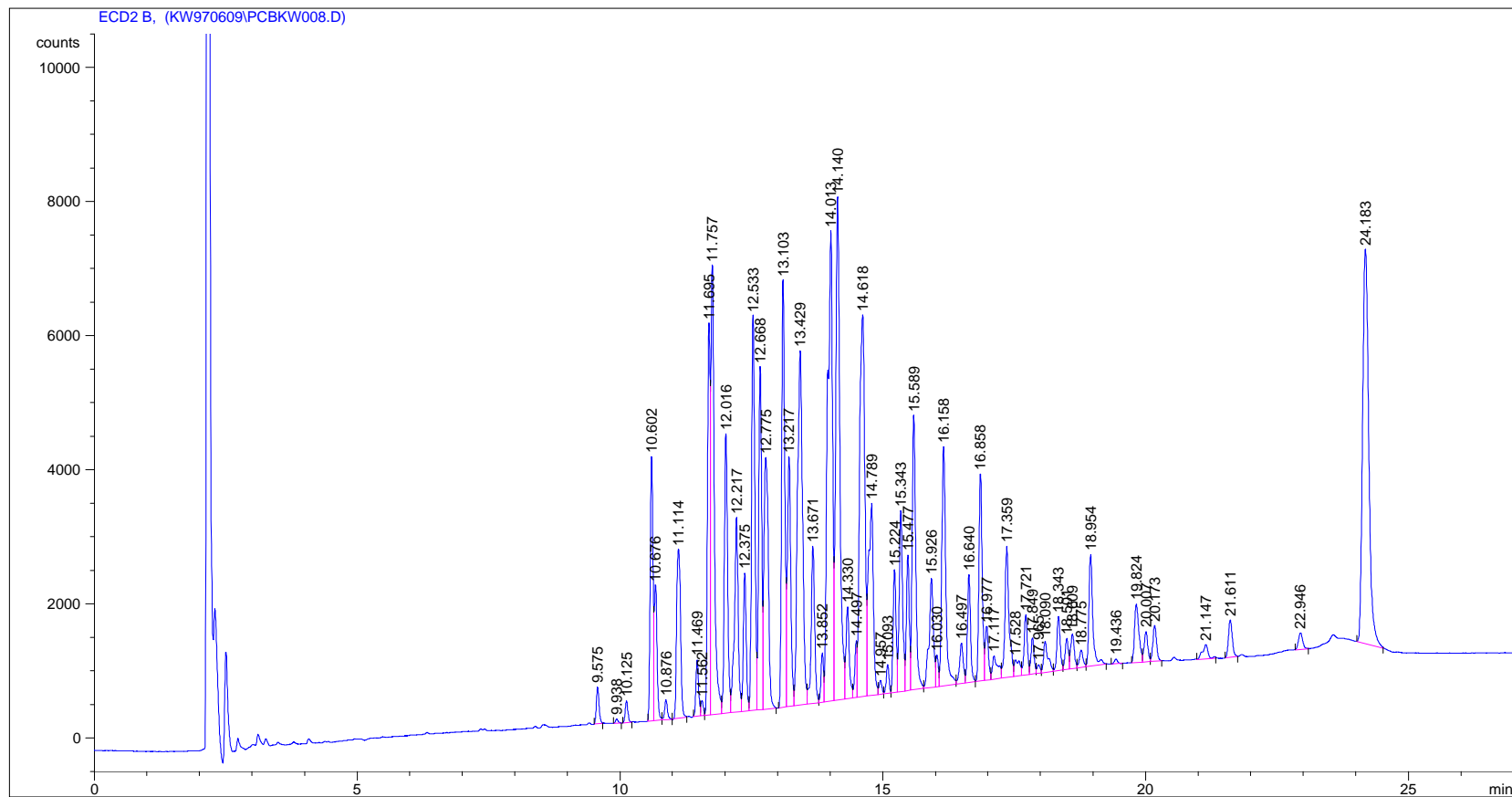
Membership vs. trial



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Chromatogram 2



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Conclusions

- The total run time was shortened from 45 to 25 minutes without any significant loss of the resolution.
- The MultiSimplex™ methods are quick, and offers a systematic optimization in a limited number of trials. You proceed in the desired direction and get off when you are satisfied.

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