OPTIMIZING THE GC TEMPERATURE PROGRAM

Resolution

\[ R_S = \frac{\sqrt{N}}{4} \left( \frac{k}{k+1} \right) \left( \frac{\alpha - 1}{\alpha} \right) \]

Efficiency \hspace{1cm} N = f (\text{gas, L, } r_c) \hspace{1cm} L = \text{Length}

Retention \hspace{1cm} k = f (T, d_f, r_c) \hspace{1cm} r_c = \text{column radius}

Selectivity \hspace{1cm} \alpha = f (T, \text{phase}) \hspace{1cm} d_f = \text{film thickness}

Temperature, the TRUMP card \hspace{1cm} T = \text{temperature}
**Column Temperature**
Developing Temperature Programs

Most powerful variable
Changes Selectivity and Retention
Natural log (ln) relationship between retention and temperature
Most to difficult predict and development
Often involves trial and error

**NOTE:** A carrier gas flow change, in a temp. program run, will affect the temperature a compound sees in that run.

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**Temperature, Retention and Resolution**

When solute \( k < 5 \)
(early eluters)

\[ T \quad \text{or} \quad d_i \quad R \]

When solute \( k > 5 \)
(later eluters)

\[ T \quad R \quad \text{or} \quad d_i \]
DEVELOPING TEMPERATURE PROGRAMS

First Step - Linear Program

Initial temperature: 40-50°C
Ramp rate: 10°C/min
Final temperature: Column's upper limit*
Final hold: Until the last peak elute

*Or until the last peak elutes from the column

DEVELOPING TEMPERATURE PROGRAMS

Linear Program
50-130°C at 10°C/min

DB-1, 15 m x 0.25 mm I.D., 0.25 µm
DEVELOPING TEMPERATURE PROGRAMS
Second Step

Change initial hold time

or

Change initial temperature

Early Eluters

When solute $k < 5$

$d_f$ \quad R

Need an increase in retention

Therefore, if early eluter ($k < 5)$

T \quad R
DEVELOPING TEMPERATURE PROGRAMS
Increase Initial Hold Time
50°C for 2 min, 50-120°C at 10°/min

DEVELOPING TEMPERATURE PROGRAMS
Increase Initial Hold Time
50°C for 4 min, 50-120°C at 10°/min
DEVELOPING TEMPERATURE PROGRAMS

Decrease Initial Temperature
40-120°C at 10°/min

DEVELOPING TEMPERATURE PROGRAMS

Increase Initial Hold Time
40°C for 2 min, 40-120°C at 10°/min
DEVELOPING TEMPERATURE PROGRAMS
Third Step

Change the ramp rate

±5°C/min per change
DEVELOPING TEMPERATURE PROGRAMS

40°C for 2 min, 40-110°C at 15°/min

DEVELOPING TEMPERATURE PROGRAMS

40°C for 2 min, 40-110°C at 5°/min
DEVELOPING TEMPERATURE PROGRAMS

Mid Ramp Holds

Isothermal portion during the temperature program

2-5 minute hold

10-30°C below elution temperature of peaks

DEVELOPING TEMPERATURE PROGRAMS

40 for 2 min, 40-70°C at 5°/min, 70°C for 2 min, (Mid Ramp Hold)
70-120°C at 10°/min
DEVELOPING TEMPERATURE PROGRAMS
40°C for 2 min, 40-110°C at 5°/min

Late Eluters
When solute $k > 5$

Need a decrease in retention
Sharper peaks even though they may be closer
DEVELOPING TEMPERATURE PROGRAMS
40°C for 2 min, 40-70°C at 5°/min, 70-130°C at 15°/min

DEVELOPING TEMPERATURE PROGRAMS
80-190°C at 20°/min

DB-WAX, 15 m x 0.32 mm I.D., 0.25 µm
DEVELOPING TEMPERATURE PROGRAMS

Lowering the Initial Temperature

**Improves resolution of earlier peaks**

*Increasing Initial Temperature Hold Time*

Similar, but smaller effect as lowering the initial temperature

Combine lower initial temperature and increased initial hold time*

*A higher initial temperature becomes feasible

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DEVELOPING TEMPERATURE PROGRAMS

Mid Ramp Hold

Sometimes improves resolution of co-eluting peaks in the middle of the chromatogram

Always causes peak broadening

Creates more complex programs
Offset retention increases by adjusting another parameter

Example:

Increase ramp rate when lowering initial temperature