

Optimal Control of Gas Chromatography Separation Using a 1D Adsorption–Desorption Model

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Abstract

Gas chromatography separates analytes through differences in their interaction with a stationary phase. This paper presents a numerical proof of concept for model-based control of two gaseous species A and B in a capillary column. The large column aspect ratio is exploited to formulate a one-dimensional model that couples axial advection-diffusion with reversible wall adsorption, while temperature-dependent desorption is described by an Arrhenius law. The model is implemented in COMSOL Multiphysics® using two Coefficient Form PDE interfaces, Domain ODEs and DAEs for the stationary-phase surface concentrations, Global ODEs and DAEs for detector-signal post-processing, and the Optimization Module. The constant carrier-gas velocity u_0 and the heating midpoint t_f are optimized to impose a prescribed outlet delay. To avoid sensitivity to time-step noise in direct peak detection, the arrival time of the retained species is estimated from a weighted temporal barycenter. A dimensionless objective minimizes the relative error between this estimate and the target time. The resulting two-parameter problem is solved with the derivative-free BOBYQA algorithm under bounded operating conditions. A preliminary time-integration study identified explicit Runge-Kutta RK34 as the most suitable solver for the convection-dominated forward model. The framework provides a COMSOL-compatible route to controlled chromatographic separation; all kinetic and transport coefficients remain proof-of-concept values requiring experimental calibration.

Keywords: gas chromatography; optimal control; adsorption-desorption; COMSOL Multiphysics®; parameter optimization; temperature programming

Introduction

Gas chromatography is a standard analytical method for separating volatile and semi-volatile compounds [1]. A sample is transported by an inert carrier gas through a column whose inner wall is coated with a stationary phase. Because each analyte repeatedly exchanges mass between the mobile and stationary phases, species with different affinities acquire different effective migration velocities and appear as distinct peaks at the detector [2,3]. Column temperature and carrier-gas velocity are therefore natural operating variables for controlling retention and elution.

Detailed three-dimensional simulations can resolve radial flow, heat transfer, and local wall transport, but their cost is difficult to reconcile with repeated model evaluations inside an optimization loop. Capillary gas chromatography columns have a very large length-to-radius ratio, which motivates a reduced one-dimensional description. Related models have shown that axial transport coupled to sorption kinetics can reproduce the principal mechanisms governing retention and peak propagation [2,3]. Open-source one-dimensional simulation tools have also been developed for gas chromatography under programmed temperature and

flow conditions [4]. The present work extends that framework toward model-based control in COMSOL Multiphysics®.

The objectives are threefold: to establish a numerically stable transient formulation for convection-dominated pulse transport; to couple two mobile-phase balances with reversible adsorption and temperature-dependent desorption; and to determine operating parameters that impose a prescribed temporal separation at the column outlet. The study is intended as a proof of concept. All kinetic and transport parameters are selected to generate physically plausible behavior rather than to represent a calibrated analyte-column pair.

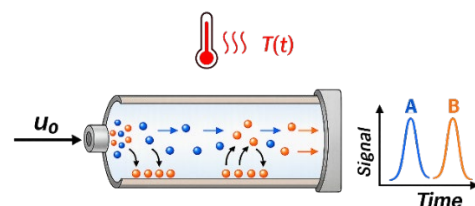


Figure 1. One-dimensional gas chromatography model with velocity and temperature control.

Figure 1 shows the control principle considered in this study. The carrier-gas velocity u_0 governs axial transport through the column, while the temperature program $T(t)$ controls the thermally activated desorption of species B. Species A, which is weakly retained, reaches the detector first, whereas species B is released later, producing two separate outlet peaks.

One-Dimensional Chromatography Model

Mobile and stationary phase balances

The physical column occupies $x \in [0, L]$, with $L = 30$ m. The numerical interval is extended beyond both ends so that homogeneous boundary conditions do not interact with the useful portion of the solution. For species $i \in \{A, B\}$, $c_i(x, t)$ denotes the mobile-phase concentration and $\Gamma_i(x, t)$ the stationary-phase surface concentration. Assuming a uniform axial carrier-gas velocity, constant axial diffusion, and a linear wall exchange law, the mobile-phase balance is

$$\frac{\partial c_i}{\partial t} + u_0 \frac{\partial c_i}{\partial x} = D_i \frac{\partial^2 c_i}{\partial x^2} - \frac{2}{R_c} r_i \quad (1)$$

where D_i is the axial diffusion coefficient, R_c is the capillary radius, and r_i is the net adsorption rate per unit wall area. The factor $2/R_c$ converts the wall flux into a source term per unit gas volume. The wall kinetics are represented by

$$r_i = k_{a,i} c_i - k_{d,i}(T) \Gamma_i, \quad \frac{\partial \Gamma_i}{\partial t} = r_i \quad (2)$$

Species A is assigned a lower adsorption coefficient than species B, so that A remains predominantly mobile while B is temporarily stored in the stationary phase. The linear law is appropriate for the present low-loading proof of concept; nonlinear isotherms can be substituted without changing the overall numerical architecture.

Temperature-dependent desorption

The desorption coefficient is evaluated from an Arrhenius expression:

$$k_{d,i}(T(t)) = A_{d,i} \exp\left(-\frac{E_{d,i}}{R_g T(t)}\right) \quad (3)$$

Here $A_{d,i}$ and $E_{d,i}$ are the pre-exponential factor and activation energy, respectively, R_g is the universal gas constant, and $T(t)$ is the prescribed column temperature. A smooth temperature step avoids introducing a discontinuity into the transient solver:

$$T(t) = T_{\text{low}} + \frac{\Delta T}{2} \left[1 + \tanh\left(\frac{t - t_T}{\tau_T}\right) \right] \quad (4)$$

where $\Delta T = T_{\text{high}} - T_{\text{low}}$. The temperature program increases from 293.15 K to 313.15 K. The optimization variable t_T sets the heating transition, whereas $\tau_T = 2$ s controls the smooth transition duration. The main proof-of-concept parameters are given by Table 1 :

L	30 m	R_c	250 μm
$k_{a,A}$	$1 \times 10^{-6} \text{ m s}^{-1}$	$k_{a,B}$	$1 \times 10^{-4} \text{ m s}^{-1}$
D_A	$1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	D_B	$8 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
$E_{d,A}$	35 kJ mol $^{-1}$	$E_{d,B}$	75 kJ mol $^{-1}$
$A_{d,A}$	$1 \times 10^8 \text{ s}^{-1}$	$A_{d,B}$	$1 \times 10^{13} \text{ s}^{-1}$

Table 1. Main physical model parameters

Initial and boundary conditions

Both species are injected as coincident Gaussian pulses centered at the inlet, with initial peak concentration $c_0 = 1 \text{ mol m}^{-3}$ and characteristic width $\sigma_x = 0.3$ m. The stationary phase is initially empty. Homogeneous Dirichlet conditions are applied at the remote boundaries of the extended numerical domain. The detector signal is represented by the local mobile-phase concentration at $x = L$. This idealized detector response is sufficient for timing optimization; a dynamic detector transfer function can be added in a subsequent model.

COMSOL Multiphysics® Implementation

The model is assembled with one Coefficient Form PDE interface for each mobile species and one Domain ODEs and DAEs interface for the surface concentration of each adsorbed species. A non-local coupling operator at $x = L$ defines the outlet signals S_A and S_B . Global ODEs and DAEs accumulate the dimensionless temporal moments B_0 and B_1 used to estimate the arrival time of species B. A Time Dependent study is nested inside a Parameter Optimization study, and parameter bounds prevent the optimizer from exploring operating conditions outside the intended numerical and physical regime. A preliminary solver study was performed with a single convected Gaussian pulse. COMSOL LiveLink™ for MATLAB® was used to compare explicit Euler, classical fourth-order Runge-Kutta, implicit Euler, and Crank-Nicolson time integration against COMSOL built-in BDF, generalized-alpha, and explicit RK34 schemes. For a 0.05 s output step, explicit Euler diverged and the low-order implicit schemes showed excessive damping or growing oscillations.

Crank-Nicolson and Runge-Kutta retained the pulse most accurately. The built-in explicit RK34 method was therefore selected for the controlled model, with strict time stepping and a nominal element size of 0.1 m.

Optimal-Control Formulation

Arrival-time definition and barycentric estimator

The outlet signals are $S_A(t) = c_a(L, t)$ and $S_B(t) = c_b(L, t)$. Because species A is weakly retained, its reference arrival time is defined analytically as $t_A = L/u_0$. Direct detection of the maximum of S_B is less robust because the reported peak time depends on the temporal output grid and can be perturbed by small numerical oscillations. The arrival of B is therefore evaluated from weighted temporal moments. Peak timing is based on a normalized weight rather than directly on c_B :

$$w_B(t) = \left(\frac{S_B(t)}{c_0} \right)^{p_{\text{Peak}}} \quad (5)$$

Here, c_0 is the reference concentration and $p_{\text{Peak}} \geq 1$ is a peak-emphasizing exponent. For $p_{\text{Peak}} = 1$, the weight follows the normalized detector signal; larger values attenuate the low-amplitude tails and concentrate the estimate around the peak apex. The barycentric arrival time is the weighted temporal mean over the simulation interval $0 \leq t \leq t_{\text{sim}}$:

$$\hat{t}_B = \frac{\int_0^{t_{\text{sim}}} t w_B(t) dt}{\int_0^{t_{\text{sim}}} w_B(t) dt} \quad (6)$$

This definition avoids a direct search for the maximum and is less sensitive to saved time levels or small numerical oscillations. In COMSOL, the two integrals are accumulated through the dimensionless global states B_0 and B_1 . The regularized barycentric estimate of the B arrival time and the analytical reference time of A are

$$\hat{t}_B = t_{\text{ref}} \frac{B_1}{B_0 + \varepsilon B}, \quad t_A = \frac{L}{u_0} \quad (7)$$

The factor t_{ref} is an arbitrary normalization scale; this factor restores the physical time dimension. With the implemented peak-emphasizing exponent $p_{\text{Peak}} = 4$, the dimensionless accumulators satisfy

$$\frac{dB_0}{dt} = \frac{1}{t_{\text{ref}}} \left(\frac{S_B}{c_0} \right)^{p_{\text{Peak}}} \quad (8)$$

$$\frac{dB_1}{dt} = \frac{1}{t_{\text{ref}}} \frac{t}{t_{\text{ref}}} \left(\frac{S_B}{c_0} \right)^{p_{\text{Peak}}} \quad (9)$$

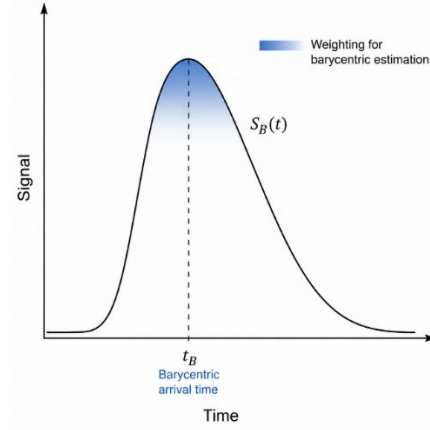


Figure 2. Barycentric peak detection.

Objective function and control parameters

The primary objective imposes a target delay τ between the barycentric arrival of B and the convective reference time of A. Normalizing by τ produces a dimensionless relative squared error:

$$J_{\text{delay}} = \frac{(\hat{t}_B - t_A - \tau)^2}{\tau^2} \quad (10)$$

The controls are the constant carrier-gas velocity u_0 and the heating transition time t_T . The set bounds are $0.08 \leq u_0 \leq 0.12 \text{ m s}^{-1}$ and $100 \leq t_T \leq 250 \text{ s}$, with initial values $u_0 = 0.1 \text{ m s}^{-1}$ and $t_T = 100 \text{ s}$. The target delay is $\tau = 176 \text{ s}$. The delay-only configuration minimizes J_{delay} .

COMSOL optimization workflow

The detector values are evaluated with a point-average coupling `aveL`, giving $S_A = \text{aveL}(c_A)$ and $S_B = \text{aveL}(c_B)$. The variables B_0 and B_1 are configured as dimensionless dependent variables in Global ODEs and DAEs, with source terms corresponding to Eqs. (8)–(9). The Parameter Optimization study minimizes J_{delay} using BOBYQA [5], with a maximum of 1000 model evaluations and an optimality tolerance of 10^{-3} . A coarse preliminary sweep over u_0 and t_T is recommended to select a robust initial point. After convergence, the optimal parameters must be copied into a separate Time Dependent study and the final chromatograms must be obtained from this direct

recomputation rather than from an internal optimizer iteration.

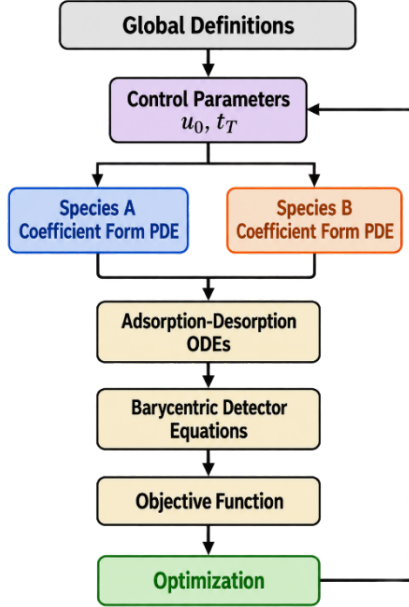


Figure 3. COMSOL optimization workflow

Figure 3 summarizes the calculation loop. Global control parameters define the two transport problems and the adsorption–desorption ODEs; the outlet signal of species B feeds the barycentric detector equations, the objective is evaluated at the end of the time-dependent study, and BOBYQA updates u_0 and t_T . In the implemented dimensionless formulation, $t_{ref} = 1$ s and $\varepsilon_B = 10^{-12}$.

Simulation window and boundary-condition control

The feasibility assessment is meaningful only if every optimization evaluation is free from artificial boundary effects. The simulation duration and the extended one-dimensional domain were therefore sized from the complete range of admissible velocities and from the requested delay. The calculation time, t_{sim} , was defined as

$$t_{sim} = \frac{L}{u_{min}} + \tau + t_{off} \quad (11)$$

where $t_{off} = 71$ s is an additional safety offset. The right boundary was then selected according to

$$x_{max} = t_{sim}u_{max} - x_{min} \quad (12)$$

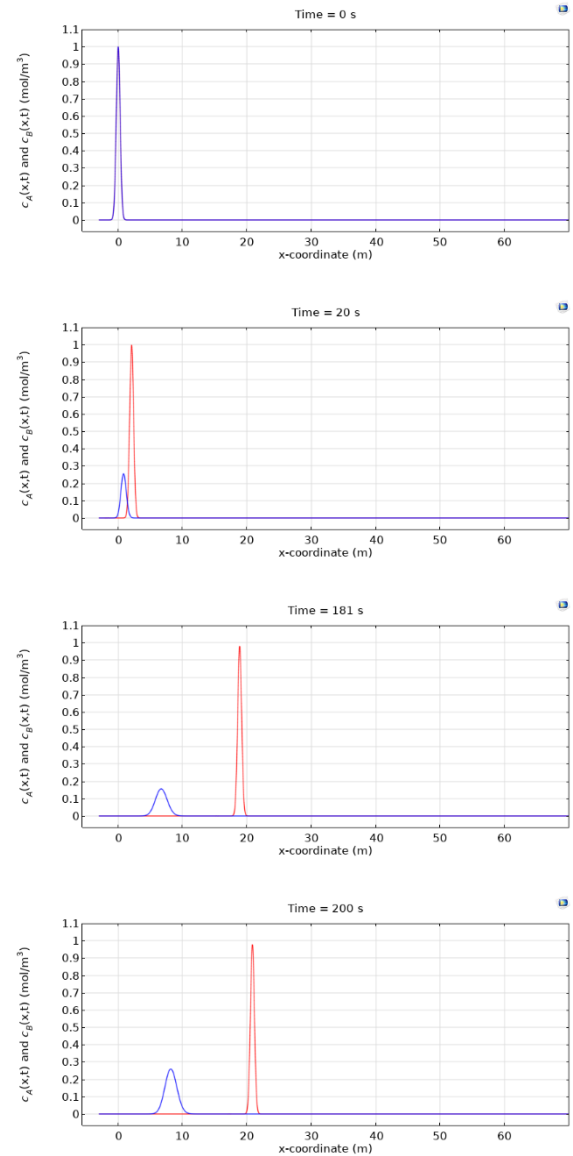
with u_{min} and u_{max} denoting the optimization bounds and x_{min} and x_{max} the numerical-domain

limits. For the present case, $x_{min} = -3$ m and $x_{max} = 77.64$ m, $t_{sim} = 622$ s. This construction allows the slowest admissible transport scenario to include the target delay and keeps the fastest pulse away from the remote boundary. Both expressions must be re-evaluated whenever the velocity bounds, the target delay, or the safety offset are changed.

Results and Discussion

Direct-model response at the optimized conditions

The final assessment was performed with a direct time-dependent computation using the optimized controls $u_0^* = 0.10419$ m s⁻¹ and $t_T^* = 181.58$ s. The axial mobile-phase concentration profiles, shown in Figure 4, provide a qualitative validation of



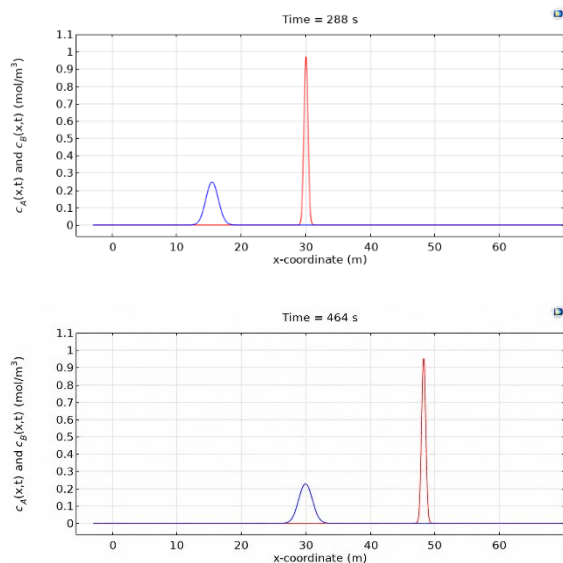


Figure 4. Axial mobile-phase concentration profiles at selected times for the optimized operating conditions

the implemented separation mechanism. Species A remains weakly retained and travels as a narrow pulse close to the carrier-gas velocity, whereas species B is strongly delayed, broadened, and attenuated by repeated exchange with the stationary phase. At approximately 288 s, the A pulse reaches the detector located at $L = 30$ m while the B pulse is still located near the middle of the column. The B pulse reaches the detector only at approximately 464 s, after species A has moved well beyond the detection point. The same sequence therefore illustrates both the internal consistency of the forward model and the optimized operating condition.

The optimized temperature program, shown in Figure 6, must be interpreted as a smooth transition rather than as an instantaneous switch. The parameter t_T is the midpoint of the hyperbolic-tangent ramp: at $t_T^* = 181.58$ s, the column temperature is 303.15 K, halfway between the low and high plateaus. On the plotted time scale, the temperature begins to depart visibly from 293.15 K roughly 10 s before this midpoint and approaches 313.15 K shortly afterward. Consequently, the mobile-phase concentration of B begins to increase slightly before t_T , because the rising temperature already increases $k_{d,B}$ and releases part of the adsorbed amount. This early increase is therefore an expected consequence of the smooth temperature law and not a premature activation of the control.

Optimization convergence and achieved delay

At the initial point specified above, the corresponding value of the delay objective was

$J_{\text{delay}} = 5.8423 \times 10^{-2}$. The first evaluations show that the heating midpoint provides the dominant coarse adjustment: at fixed $u_0 = 0.1 \text{ m s}^{-1}$, increasing t_T to 160 s reduced the objective to 2.5796×10^{-3} . Subsequent coupled updates of the velocity and heating midpoint refined the timing relationship. As shown in Table 2, after 19 model evaluations, the best parameter pair was $u_0^* = 0.10419 \text{ m s}^{-1}$ and $t_T^* = 181.58$ s, with $J_{\text{delay}} = 2.6874 \times 10^{-10}$. The nonmonotonic intermediate values are consistent with the exploratory trust-region steps used by the derivative-free algorithm; the relevant result is the progressive reduction of the best attained objective by more than eight orders of magnitude. The convergence history is shown in Figure 5.

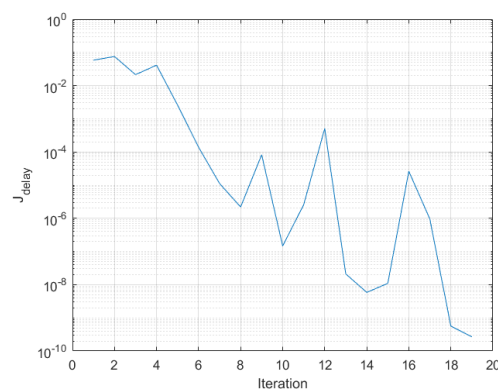


Figure 5. Convergence of the dimensionless delay objective during the BOBYQA iterations

Iteration	u_0	t_T	J_{delay}
1	0.10000	100.00	0.058423
2	0.10800	100.00	0.075354
3	0.10000	130.00	0.021383
4	0.092000	100.00	0.041291
5	0.10000	160.00	0.0025796
6	0.092293	168.05	1.3869E-4
7	0.099934	176.93	1.1147E-5
8	0.10761	185.35	2.1922E-6
9	0.11499	196.97	8.2394E-5
10	0.10442	181.98	1.4707E-7
11	0.10754	186.23	2.5695E-6
12	0.10413	188.60	5.1131E-4
13	0.10303	180.01	2.1153E-8
14	0.10389	181.15	5.8418E-9
15	0.10360	180.78	1.0980E-8
16	0.10403	179.75	2.6201E-5
17	0.10428	181.38	9.5585E-7
18	0.10426	181.67	5.6383E-10
19	0.10419	181.58	2.6874E-10

Table 2. BOBYQA optimization history for u_0 , t_T , and the delay objective J_{delay} for $\tau = 176$ s

For the optimized velocity, the analytical reference arrival time of species A is $t_A^* = L/u_0^* = 287.94$ s. With the prescribed delay $\tau = 176$ s, the corresponding target arrival time of species B is $t_A^* + \tau = 463.94$ s. The achieved delay differs from the prescribed value by only 2.9×10^{-3} s. Within the accuracy of the transient computation and the barycentric estimator, the requested delay is therefore achieved.

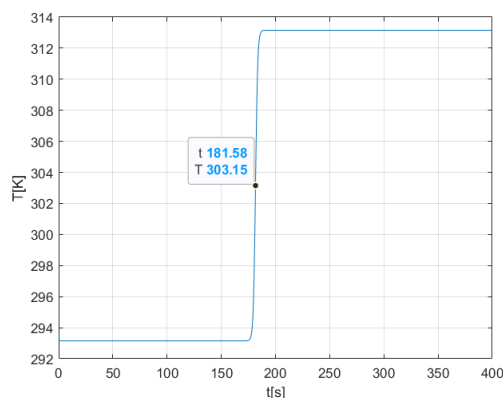


Figure 6. Optimized temperature program;
 $t_T = 181.58$ s is the midpoint of the smooth
293.15–313.15 K transition.

Physical attainability of the prescribed delay

A central outcome of the study is that the target delay cannot be selected independently of the transport, sorption, temperature program, and admissible control bounds. The optimizer can identify a parameter pair that achieves the prescribed delay only when the requested value of τ lies within the physically reachable range of the model. If the target is not attainable, the calculation should converge to a nonzero residual or to a control bound; such a result indicates target infeasibility rather than optimizer failure. In the present proof of concept, $\tau = 176$ s is attainable, as demonstrated by the near-zero final objective. The purpose of the optimization procedure is therefore twofold: the optimization procedure acts as a control design tool and as a numerical feasibility test for a proposed chromatographic delay.

Limitations and Next Steps

The present results demonstrates that the prescribed delay optimization is successful when a physically feasible target is supplied, however the reachable delay interval is not automatically determined. A first extension should map the minimum and maximum attainable delays under the selected velocity and temperature bounds, for example by combining coarse parameter sweeps, continuation in τ , and constrained optimization. The numerical

domain and simulation time rules should also be incorporated automatically so that each candidate target is evaluated with valid remote-boundary conditions.

An ideal chromatographic objective would balance timing and detectability rather than minimizing delay error alone. Candidate terms to investigate include a smooth penalty for low B-peak amplitude, an overlap integral between the two outlet signals, penalties for excessive peak broadening, and regularization of rapid or energy-intensive control changes. One possible future problem is to minimize the physically achievable phase shift while imposing a minimum B-peak amplitude and an acceptable overlap or resolution criterion. The smooth peak height accumulator proposed previously could provide one component of such a cost function. If this path is explored, a dedicated sensitivity study is required for the weighting of the accumulator and its interaction with the timing term.

Further developments should include calibration of the adsorption and desorption coefficients against measured chromatograms, assessment of nonlinear adsorption at higher loading, and evaluation of pressure drop, gas compressibility, radial transport, and detector dynamics. These additions are required before the optimized controls can be interpreted as an instrument-ready operating program.

Conclusions

The one-dimensional COMSOL model reproduced the selective retention and thermally activated release required for controlled gas-chromatographic separation. Starting from $u_0 = 0.1$ m s⁻¹ and $t_T = 100$ s, BOBYQA identified the optimal values $u_0^* = 0.10419$ m s⁻¹ and $t_T^* = 181.58$ s after 19 model evaluations. The target delay $\tau = 176$ s was matched to within approximately 2.9×10^{-3} s, reducing the dimensionless delay objective from 5.8423×10^{-2} to 2.6874×10^{-10} .

The study also shows that optimization performance cannot be separated from physical attainability and numerical domain design. The prescribed delay must lie within the range permitted by the retention dynamics and control bounds, while the simulation duration and extended domain must remain valid for every candidate solution. The present calculation establishes the intended proof of concept: the COMSOL-based workflow identifies operating parameters that realize the requested separation, as long as the latter is physically reachable. For the present discretization, comprising 808 mesh nodes, the complete optimization required 2 h 05 min 8 s on a Dell Precision 7540 laptop equipped with 32 GB of RAM and a six-core Intel Core i7-9850H processor operating at a nominal frequency of

2.6 GHz. This computational cost remains compatible with an offline optimization framework, while highlighting the importance of model reduction and efficient numerical settings for future extensions. Determining the minimum feasible delay while preserving a detectable B peak is the principal next step.

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