Transient Heating and Cooling in a Packed Bed with Fluid Flow for Controlling Solute Adsorption

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INTRODUCTION

Reversed phase liquid chromatography is an analytical chemistry technique used to physically separate compounds in complex mixtures. Separation is achieved by developing a two-phase equilibrium between a liquid mobile phase pumped through a bed of small, “stationary” silica-based particles. The particle surface is modified with nonpolar octadecyl alkylsilanes. Analyte adsorption to the particle is based on its affinity for the hydrophobic surface. Affinity increases as column temperature decreases. Temperature assisted solute focusing (TASF) uses this temperature dependence to concentrate samples by loading analyte bands onto a cold pre-column. The sample is released by heating the column. Heating must be both fast and uniform throughout the precolumn to minimize temperature-induced band broadening. An array of high power Peltier devices was used to control temperature inside the custom low thermal mass stainless steel TASF pre-column.

We developed a finite element model of the device to determine the limits of physical geometry and experimental parameters. Analyte adsorption was modeled in the precolumn using thermodynamic parameters for four compounds: uracil, ethylparaben, propylparaben, and butylparaben (Figure 1). This work provides direct information about heat flow in the device. Most importantly, it provides information about the temperature profile across the diameter of the device. Temperature variation across the diameter of the device leads to radial velocity inhomogeneities for solute bands, degrading performance.

	Uracil	Ethylparaben	Propylparaben	Butylparaben
k’ 0 °C	0	15.4	40.9	112.9
k’ 80 °C	0	3.7	8.0	17.2

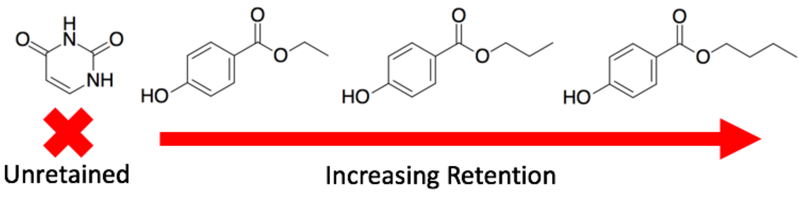

Figure 1: Structures and retention factors of model compounds at 0º and 80º C

$$\bar{v} = \frac{u}{1+k'}$$

Equation 1: Analyte velocity
$\bar{v}$ = average band velocity
u = average liquid velocity
k’ = retention factor

COMPUTATIONAL METHODS

The setup consists of a temperature controlled steel device with fluid flow through the center. Fluid first enters through an open tube, passes through a porous frit, porous column, and another porous frit, before exiting through an open tube (Figure 2A). Adsorption occurs in the porous column.

The physics modules used are Heat Transfer in Porous Media, Free and Porous Media Flow, and Transport of Dilute Species in Porous Media. The Heat Transfer Module applies a heat source boundary on the top and bottom of the device to represent the Peltier devices used and constant temperature at the fluid inlet. The Free and Porous Media Flow module accounts for the fluid flow in the open tubes and the porous media. The Transport of Dilute Species in Porous Media accounts for temperature dependent adsorption and band spreading for each of the analytes on the column (Equation 2A-2C).

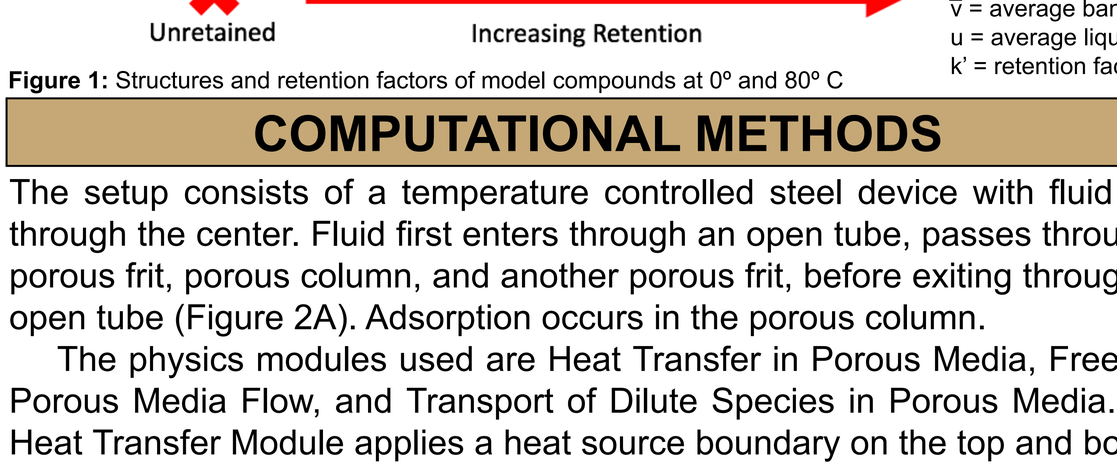

Figure 2: Cross-section view of pre-column device
A: Parallel to flow; **B:** Perpendicular to flow

Equation 2A: Transport of Dilute Species

$$\left(\varepsilon_p + k_p\right)\frac{\partial c_i}{\partial t} + \nabla\cdot\left[-\mathscr{D}\,\nabla c_i + u c_i\right] = 0$$

Equation 2B: Dispersion

$$\mathscr{D} = \mathscr{D}\left(\phi, T, \eta, d_p, u_e, K\right)$$

Equation 2C: Adsorption

$$k_p = K\left(T, \Delta H, k'\right)\left(1-\varepsilon_p\right)$$

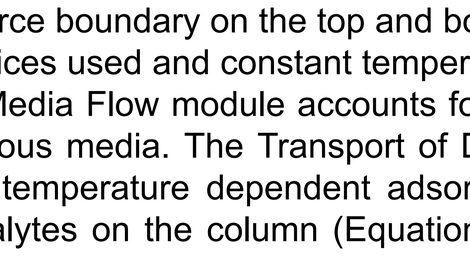

Figure 3: Three dimensional view of pre-column device

RESULTS

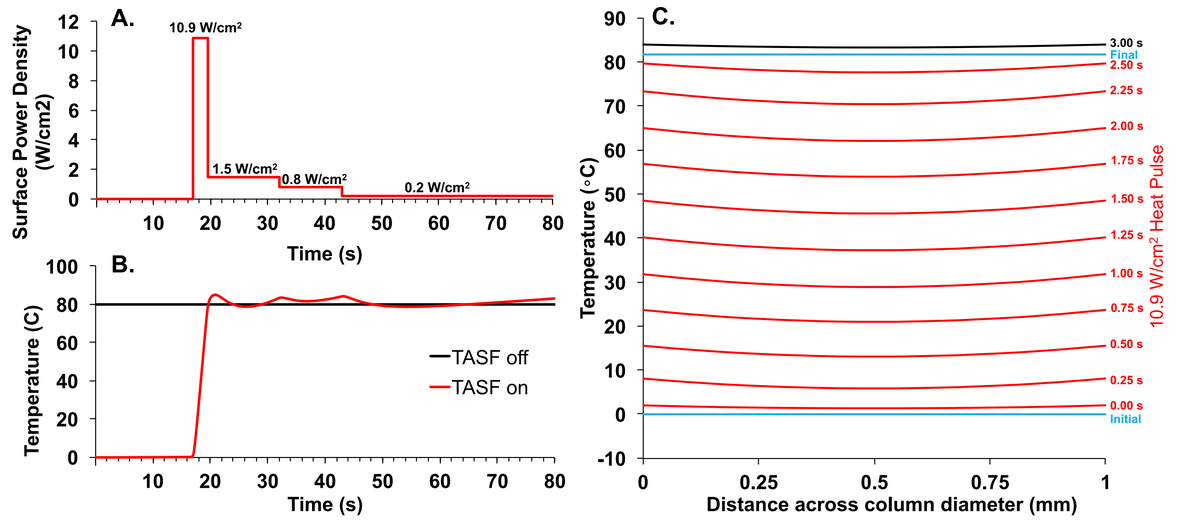

Figure 4A: Boundary heat source power density graph, **B:** Temperature profile at center of column, **C:** Temperature profile across column diameter between Peltier devices

Column temperature was maintained using a user-defined heat source boundary (Figure 4A). Figure 4B shows the temperature profile at the center of the column. Figure 4C shows the temperature profile across the diameter of the column at various time points before, during, and after the 2.5 s, 10.9 W/cm^2 heat pulse to heat the column from 0 ºC to 80 ºC.

Simulation:

Experiment:

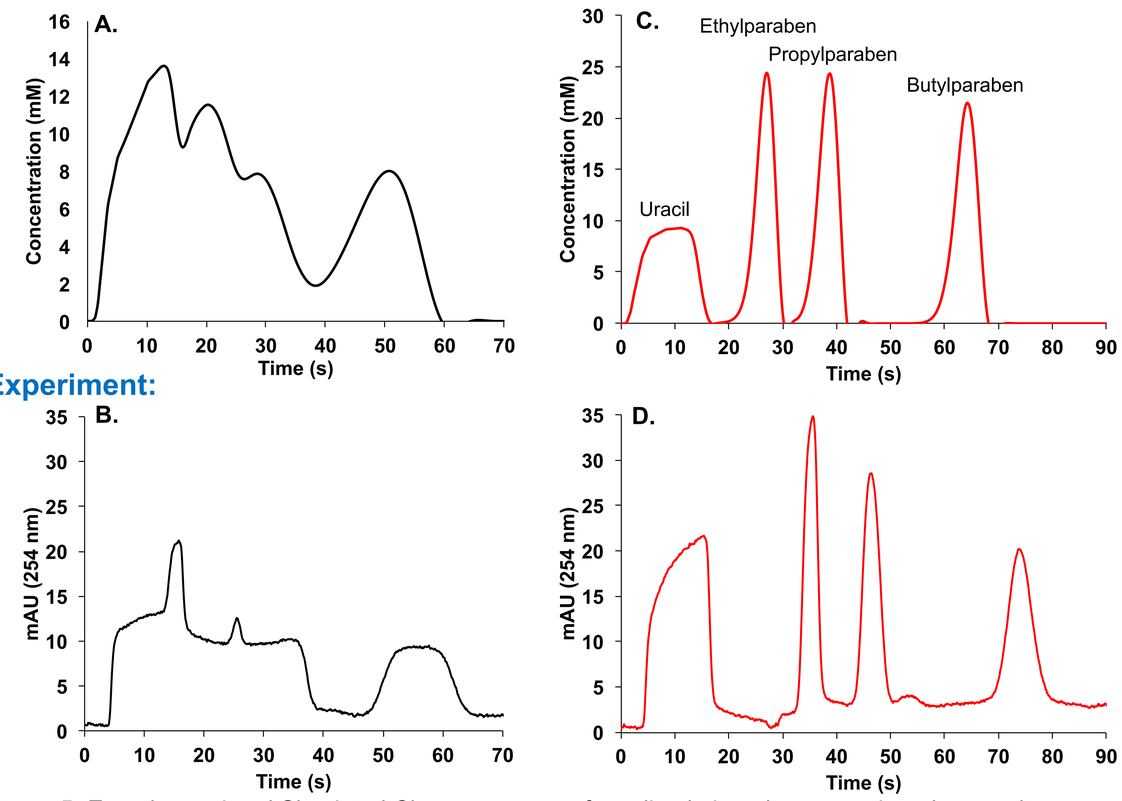

Figure 5: Experimental and Simulated Chromatograms of uracil, ethylparaben, propylparaben, and butylparaben mixtures: **5A:** Isothermal COMSOL Simulation; **5B:** Isothermal Experiment; **5C:** TASF Simulation – Peaks normalized to isothermal peaks due to analyte loss from adsorption isotherm; **5D:** TASF Experiment

Figure 5 shows a comparison between simulated and experimental chromatograms. The COMSOL chromatograms were generated from a surface average at 0.5 mm into the column’s porous outlet frit. From left to right, the peaks are uracil, ethylparaben, propylparaben, and butylparaben. Retention and band spreading for the simulated chromatograms reflect experiment and chromatographic theory.

CONCLUSION

The finite element model presented has allowed for prediction of important experimental parameters and optimization of device geometry. Simulations were a vital tool for determining whether heat transfer rates were fast enough to support a given column diameter, length, flow rate, and analyte choice. This model, complete with fluid flow, heat transfer, and mass transport calculations allowed us to explore different device geometries, column diameters, flow rates, and analyte mixtures using different thermodynamic parameters to further optimize separations using a TASF pre-column device.

ACKNOWLEDGEMENTS

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REFERENCES

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