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GasChromatographySimulator.jl

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Software

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Summary

Gas chromatography (GC) is a technique used in analytical chemistry to separate a mixture of vaporizable substances by injecting the mixture into a gas stream (mobile phase), which passes along a tube, called column, of length L and diameter d. The column is coated with a stationary phase of a film thickness d_f. The substances of the mixture interact with the stationary phase by partition between mobile and stationary phase, resulting in different effective velocities of the substances. At the end of the column the substances are registered in a detector at different times, called retention times, and with different peak widths, resulting in a chromatogram. GC is used for qualitative and quantitative analysis, e.g. in petrochemistry, food chemistry, environmental analytics, and forensic science.

The modeling of GC separations is used for the prediction of retention times and widths of the signals. With these results, the separation of substances can be evaluated via the resolution of neighboring substance peaks in the chromatogram. Such simulations are of interest for method development, especially in multidimensional GC (Gaida et al., 2021; Hou et al., 2018; Jaramillo & Dorman, 2020) and for the evaluation of new techniques, like thermal gradient GC (Leppert, Müller, et al., 2020) or stationary phase thickness gradients (Li et al., 2020). While the presented package only models one-dimensional GC separation, it can be used as the base for a multi-dimensional GC separation.

Statement of need

`GasChromatographySimulator.jl` is a Julia package (Bezanson et al., 2017) to simulate the separation of a number of substances in a GC system with programmed temperature $T(t)$, programmed inlet pressure $p_{\text{in}}(t)$, and programmed flow $F(t)$. In principle, the outlet pressure $p_{\text{out}}(t)$ can also be programmed. The package also allows for spatial changes of the diameter of the GC column $d(x)$, of the film thickness of the stationary phase $d_f(x)$ and of the temperature $T(x)$. The simulation is based on solving a system of ordinary differential equations (ODE) for the migration of the substances through the GC system $t(x)$ and for the development of the temporal variance of the substance distribution $\tau^2(x,t)$.

The ODE system for migration $t(x)$ and temporal variance development $\tau^2(x,t)$ is:

$$\frac{dt}{dx} = r(x,t)$$

and

$$\frac{d\tau^2}{dx} = H(x,t)r(x,t) + 2\tau^2(x,t)\frac{\partial r(x,t)}{\partial t}$$

with r the inverse substance velocity ($r = 1/u$) and H the local plate height, (Leppert, Blumberg, et al., 2020), on the interval of $0 \leq x \leq L$, where L is the length of the column. The basic equations building the model are presented in an earlier publication (Leppert, Müller, et al., 2020) and can be found in the documentation of the package. This ODE system is solved by using the Julia packages `OrdinaryDiffEq.jl` and `Integrals.jl`, part of

`DifferentialEquations.jl` (Rackauckas & Nie, 2017) and `ForwardDiff.jl` (Revels et al., 2016). Also the packages `Interpolations.jl` and `ChemicalIdentifiers.jl` are used.

`GasChromatographySimulator.jl` provides an interface to define a GC system consisting of:

- column (length, diameter, film thickness, type of stationary and mobile phase, optional spatial change of diameter and/or film thickness)
- program (temperature and pressure program, optional thermal spatial change)
- substance parameters (thermodynamic parameters, diffusion coefficient, time of injection, width at injection)
- additional options (e.g. tolerances, algorithm for solving ODEs, model of viscosity)

By providing the thermodynamic parameters (Blumberg, 2017) for the interaction of substances and stationary phase, which can be estimated by isothermal GC measurements, the separation of mixtures of substances can be simulated for a wide range of GC systems.

Figure 1 shows the simulation of a separation with thermal gradient of n-alkanes and compares it to a real measurement from (Leppert, Müller, et al., 2020).

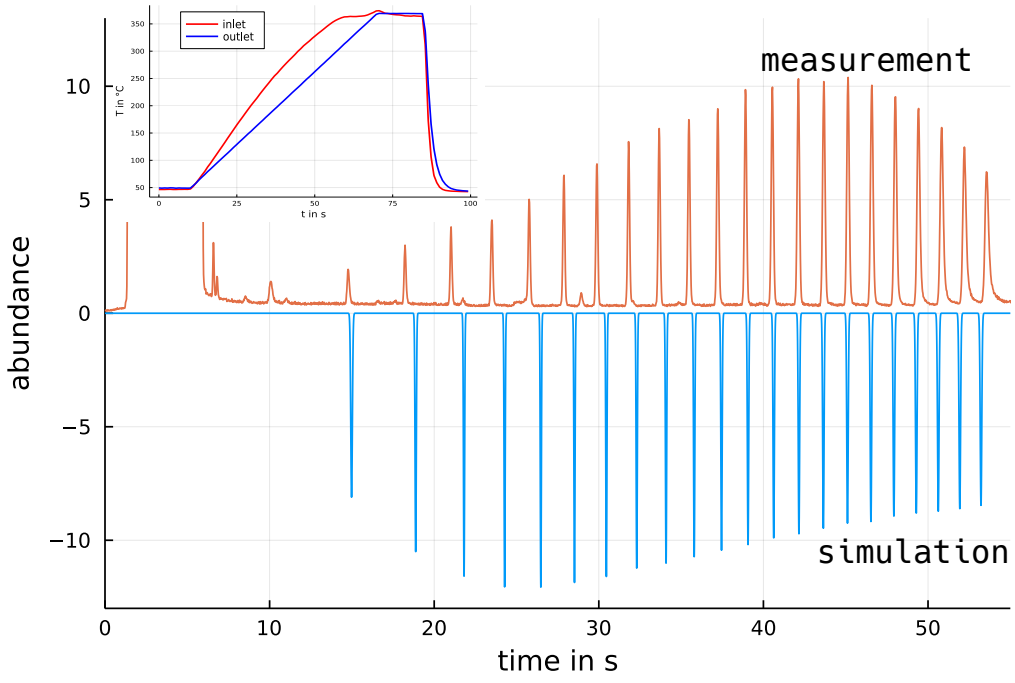

Figure 1: Comparison of measured and simulated thermal gradient GC separation. For more details, see the examples section in the documentation.

A collection of `Pluto.jl` notebooks (Plas et al., 2022) are made available together with this package to provide a simple template to setup and simulate arbitrary GC systems for users with less coding experience.

This package is unique because it allows simulation of GC systems with non-uniform diameter, stationary film thickness and temperature. Available simulations, such as those published in supplementary material for (Gaida et al., 2021) or (Hou et al., 2018), are only able to simulate conventional GC. A commercial but free-to-use simulation software is Pro EZGC by Restek Corporation (Restek Corporation, n.d.), which only allows the simulation of conventional GC for defined stationary phases (produced by Restek) and defined substances.

A full investigation of the properties of thermal gradient GC using `GasChromatographySimulator.jl` is in preparation. Also a project `ThermodynamicDataEstimator` to determine the thermody-

namic parameters of substances based on optimization to match measured retention times in temperature programmed GC, similar to (Hou et al., 2018), is in development. The package `GasChromatographySimulator.jl` is a foundation for this project.

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