# ALS SCHEME USING EXTENT-BASED CONSTRAINTS FOR THE ANALYSIS OF CHEMICAL REACTION SYSTEMS

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Multivariate curve resolution via alternating least squares (ALS) is used to resolve the concentration profiles $\mathbf{C}$ and the pure component spectra $\mathbf{E}$ of $S$ species from the multivariate absorbance data $\mathbf{A}$, assuming the bilinear model $\mathbf{A} = \mathbf{C}\,\mathbf{E}$. Due to the possible permutations of profiles and the presence of intensity and rotational ambiguities, soft constraints such as nonnegativity of $\mathbf{C}$ and $\mathbf{E}$ as well as unimodality, monotonicity, closure, and local rank selectivity of $\mathbf{C}$ are typically used to obtain tighter solution bounds for $\mathbf{C}$ and $\mathbf{E}$ [1].

In addition, hard constraints in the form of kinetic models are also often used. Unfortunately, these models are subject to structural plant-model mismatch and parametric uncertainty, which weakens their impact. As an alternative, this paper proposes to use constraints based on variant states called extents. The computation of these extents does not require any information on the rate processes, that is, $\mathbf{x}(t) = \mathbf{T}\,\mathbf{n}(t)$, with $\mathbf{x}(t)$ and $\mathbf{n}(t)$ the vectors of extents and numbers of moles at time $t$, respectively, and $\mathbf{T}$ a matrix known from the reaction stoichiometry, the inlet composition and the initial conditions [2]. Expressing the $S$ concentrations in terms of $d$ extents and $q = S - d$ invariants reduces the dimensionality of the problem from $S$ to $d$. Each column of the extent matrix $\mathbf{X}$ describes the extent of a single rate process, for example of a reaction or an inlet flow. It turns out that the unknown concentration matrix $\mathbf{C}$ can be expressed in terms of the lower-dimensional matrix $\mathbf{X}$ as $\mathbf{C} = \mathbf{V}^{-1}\mathbf{X}\,\mathbf{T}^{-\mathrm{T}}$, where $\mathbf{V}$ is a diagonal matrix containing the volume profile. Since each column of $\mathbf{X}$ describes a single rate process, additional constraints can be enforced on $\mathbf{X}$ such as monotonicity and convexity/concavity [3]. Furthermore, the $q$ invariant relationships can be used as constraints in the least-squares problem. As a consequence, the use of extents in ALS reduces the ambiguity between $\mathbf{C}$ and $\mathbf{E}$, yielding faster convergence and tighter solutions.

The use of extent-based constraints also opens up new perspectives for hard-soft ALS methods, since hard kinetic models can be identified individually (that is independently of the other rates) for some selected processes, while soft extent-based constraints are used for the unknown processes. Another feature involves the possibility of initializing or constraining the ALS scheme with a concentration submatrix (of dimension at least $S \times S$) estimated from multiple experiments performed under well-designed conditions and local-rank information. Together with the corresponding absorbance data, this submatrix can efficiently replace the traditional initialization via factor analysis and be used to compute a better initial estimate of $\mathbf{E}$.

After a brief review of the mathematical properties of extents for batch and open reactors, this talk will present the modified ALS scheme and illustrate it via simulated examples.

**References:**

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