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# Unified Design of chromatographic processes with timed events: Separation of ternary mixtures

Tuomo Sainio

*School of Engineering Science, Lappeenranta University of Technology, Skinnarilankatu 34, FI-53850 Lappeenranta, Finland*

## HIGHLIGHTS

- A method for designing and analyzing chromatographic separation processes.
- New compatible operating parameters enable comparison of different processes.
- Ternary systems investigated using equilibrium theory and numerical simulations.
- Operating parameter limits derived for complete separation in batch, JO, and 3W-ISMB.

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ABSTRACT

An important unifying property of single and multicolumn chromatographic processes, whether discontinuous or continuous, is that they are based on timed events. The Unified Design method was revised by defining three kinds of events (cut event, fixed-bed event, SMB event). Binary and multicomponent separations in various process configurations, from single column batch to complex multicolumn units, can readily be described as combinations of such events. New dimensionless parameters were introduced to describe these events, and their combinations were used as operating parameters for different processes. Transformations between physical and dimensionless operating parameters were introduced. Regions of feasible operating parameters for complete separation of ternary mixtures with linear isotherms were derived for batch chromatography and two SMB-type processes (Japan Organo, 3W – ISMB) using the equilibrium theory. It was shown that these can be visualized and overlaid on the Unified Design operating parameter plane, which enables their direct comparison. It was found that in many cases the complete separation regions of apparently very different process schemes are identical or exhibit strong similarities. This indicates that it should be possible to transfer the operating point from one process mode to another without affecting the product purity if column efficiency is very high.


## 1. Introduction

The Unified Design method (Siitonen and Sainio, 2015) was recently introduced to present the design of several common chromatographic process options in a manner similar to the so-called Triangle Theory method (Storti et al., 1993) of counter-current simulated moving bed (SMB) chromatography. The key idea is that cut times, which are used as physical operating parameters for single column processes, can be presented as dimensionless operating parameters of the same type as SMB flow rate ratios, and thus plotted on the same operating parameter plane. Useful definitions for such parameters were introduced for single column batch chromatography, steady state recycling chromatography (SSR) as well as for counter-current and cross-current SMB and TMB (Siitonen and Sainio, 2015). Since the operation of apparently quite different chromatographic process modes can be presented in the same unified form, the Unified Design method facilitates – at least in principle – transferring existing designs from one process mode to another mode. This is particularly useful because a complicated but powerful process mode can be designed by considering a much simpler process mode.

Independent of Siitonen and Sainio (2015), also Nicoud (2015) discovered a strong analogy between the optimal operating points of batch and counter-current SMB chromatography under ideal conditions. Nicoud showed that, when normalized to the volume of adsorbent in the column, the volume of fresh feed that gives "touching bands" operation of batch chromatography equals the feed flow to solids flow ratio at the vertex of the complete separation region in SMB chromatography. Three of the four design parameters of SMB can be read from a single "touching bands" chromatogram under ideal conditions.

*E-mail address:* Tuomo.Sainio@lut.fi

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**Nomenclature**

| | |
|---|---|
| $A$ | cross-sectional area of the column, $m^2$ |
| $c$ | liquid phase concentration, mol $m^{-3}$ |
| $F$ | solid-to-liquid phase ratio in the column, dimensionless |
| $H$ | Henry constant, dimensionless |
| $\bar{H}$ | modified Henry constant, $\bar{H}_j = F^{-1} + H_j$, dimensionless |
| $h$ | event index in the case of consecutive FB events, dimensionless |
| $l$ | propagation distance during an event relative to the length of the column, dimensionless |
| $l'_{SMB}$ | propagation distance during an SMB event before the switch occurs |
| $m$ | number of cycles in 3W − ISMB, see Appendix C |
| $N_{col}$ | total number of columns in SMB or JO process, dimensionless |
| $N_k$ | number of columns in zone $k$ in SMB or JO process, dimensionless |
| $N_{SMB}$ | number of SMB events in the repeating sequence of the process, dimensionless |
| $Q$ | volumetric flow rate, $m^3 s^{-1}$ |
| $S$ | auxiliary dimensionless operating parameter, dimensionless |
| $s$ | dimensionless operating parameter, dimensionless |
| $\hat{s}$ | cumulative operating parameter used in case of consecutive FB events, dimensionless |
| $t$ | time, s |
| $t_0$ | elution time of a non-adsorbing component, s |
| $u$ | interstitial liquid flow rate, m $s^{-1}$ |
| $V$ | volume, $m^3$ |
| $z$ | axial coordinate in the column, m |

*Greek symbols*

| | |
|---|---|
| $\varepsilon$ | bed porosity, dimensionless |
| $\lambda$ | distance from the end of zone relative the length of a single column, dimensionless |
| $\mu$ | number of SMB events taken in 3W − ISMB before the rear of C enters zone I, see Appendix C |

*Subscripts*

| | |
|---|---|
| col | column |
| cut | cut event |
| EL | elution |
| FB | fixed-bed event |
| j | component index; zone index; operating parameter index |
| JO | the Japan Organo process |
| SMB | simulated moving-bed event or process |
| switch | port switching interval in SMB or JO |
| W | 3W − ISMB process |

*Superscripts*

| | |
|---|---|
| L | liquid phase |
| F | feed |
| FF | fresh feed |

The Unified Design method provides even more information about the operating parameter space because the entire feasible range of dimensionless operating parameters can be visualized. While the touching bands operation of batch chromatography corresponds to the vertex of the complete separation region of SMB, any feed volume below this value gives two operating points on the sides of the triangle. Closed-form expressions for the complete separation region of common single column operations were derived and found to be identical to those of SMB/TMB (Siitonen and Sainio, 2015). This is significant as robust design and operation of SSR chromatography, for example, has been complicated by the fact that the previous design methods (Kaspereit and Sainio, 2011; Sainio and Kaspereit, 2009) provide only a single operating point and no information about safety margins of the operating parameters. By using the Unified Design method, a robust operating point for SSR (even when integrated with a solvent removal unit to concentrate the recycle stream) can be selected by moving from the optimal operating point towards the interior part of the feasible operating parameter region (Siitonen et al., 2015).

Here we present a new, more general terminology and notation for the Unified Design method. The new formulation is based on identifying the use of timed events (see Section 2) as the unifying feature of chromatographic single and multicolumn processes. It is shown that various chromatographic processes can be constructed by combining three kinds of events in an appropriate order. The events are described with a set of compatible dimensionless Unified Design operating parameters. Compatibility means that operating parameters of process configurations are obtained as linear combinations of the operating parameters of the events. In this view, there is a much stronger analogy between single column batch chromatography and counter-current SMB than between the SMB and the TMB. This is because the TMB process, as well as the annular chromatography process, has no timed events.

Until now, only binary separations have been considered in the context of the Unified Design method. Apart from batch chromatography, the chromatographic process options used for ternary and multicomponent separations are advanced multicolumn schemes (Kaspereit, 2009). Several modifications to the classical SMB technology have been proposed to overcome its inherent drawback of splitting the feed stream into two product streams only. The two main types are SMB cascades and single SMB units with discontinuous feeding and/or product collection. In an SMB cascade, two (for ternary) or more conventional SMB units (Nowak et al., 2012) or their modifications (Jermann et al., 2015) are coupled. If the first SMB unit is operated such that it produces pure extract (raffinate) stream, the impure raffinate (extract) is used as the feed to the second SMB unit. Design and analysis of cascades is straightforward using the Triangle Theory when the process has continuous feeding (Nowak et al., 2012; Wei et al., 2012).

The Japan Organo process, which uses a four-zone SMB arrangement, is perhaps the most well-known example of a single SMB unit with discontinuous feeding and/or product withdrawal. Discontinuous feeding and/or product withdrawal can be employed also in two-zone (Jo et al., 2007; Hur and Wankat, 2005) and five-zone (Mun, 2010; Mun, 2011) SMBs, as well as in several modifications of the I-SMB process (Jermann et al., 2012) that have shown potential for ternary separations. In the latter concepts, each port switching interval is divided into two or more substeps where feed and product withdrawal are discontinuous. In the JO process, a single feeding step is followed by a full cycle (or at least several switches) of conventional SMB-type port switches. Nowak et al. (2012) concluded that “since the JO process is a complex pseudo-SMB technique, in which the step equivalent to SMB separates only the strongest and the weakest adsorbed compounds,