Adsorption (2007) 13: 541–567
DOI 10.1007/s10450-007-9035-3

Theoretical investigation of the adsorption of a binary mixture in a chromatographic column using the nonlinear frequency response technique

**Milica Ilić · Menka Petkovska ·
Andreas Seidel-Morgenstern**

Received: 30 April 2007 / Revised: 19 July 2007 / Accepted: 23 July 2007 /

Abstract The nonlinear frequency response of a chromatographic column for the adsorption of two dissolved components is analyzed using the concept of higher order frequency response functions (FRFs) which is based on the Volterra series and generalized Fourier transform. By applying this concept a nonlinear model of a system is replaced by an infinite series of the FRFs of the first, second, etc. order. The FRFs up to the third order are derived theoretically starting from the equilibrium-dispersive model, which is used for description of a chromatographic column, and applying the harmonic probing method. The functions that relate outlet concentration changes of each component to the corresponding inlet concentration changes are derived. At the inlet of a chromatographic column, it is considered: (a) the concentration change of one of the components keeping the concentration of the other component constant and (b) the concentration change of both components keeping their ratio constant. The FRFs are calculated numerically for different steady-state concentrations and relative mixture compositions. It has been found that, despite certain differences in initial conditions, the FRFs exhibit similar behavior. For higher frequencies, the amplitudes of the FRFs tend to zero and phases to $-\infty$. In the low frequency range, which is of interest for investigation of equilibrium parameters, these functions have similar behavior, but tend to different asymptotic values. Correlations between coefficients of competitive adsorption isotherms, i.e. partial isotherm derivatives, and the derived FRFs are established. This theoretical result offers the potential to use the analysis of the nonlinear frequency response of a chromatographic column for estimation of competitive adsorption isotherms.

Keywords Binary mixture · Competitive adsorption isotherm · Nonlinear frequency response · Higher order frequency response functions

Abbreviations

$\tilde{a}_{ij}$	Coefficient of the dimensionless competitive adsorption isotherm
$\tilde{b}_{ij}$	Coefficient of the dimensionless competitive adsorption isotherm
b_L, b_S	Parameters of the adsorption isotherm, $1/g$
c	Dimensionless concentration in the liquid phase
$\tilde{c}_{ij}$	Coefficient of the dimensionless competitive adsorption isotherm
C	Concentration in the liquid phase, g/l
C_s	Steady-state concentration in the liquid phase, g/l
D_{app}	Apparent dispersion coefficient, cm^2/s
f	Dimensionless factor
$F_n(x, \omega_1, \omega_2, \ldots, \omega_n)$	n-th order frequency response function that relates the concentration change of the component 2 at distance x from the

---

M. Ilić · A. Seidel-Morgenstern (✉)
Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany
e-mail: anseidel@vst.uni-magdeburg.de

M. Petkovska
Department of Chemical Engineering, Faculty of Technology and Metallurgy, Belgrade, Serbia

A. Seidel-Morgenstern
Otto von Guericke University, Chair of Chemical Process Engineering, Magdeburg, Germany

	column inlet with the inlet concentration change
$F_n^*(\omega_1,\omega_2,\ldots,\omega_n)$	n-th order frequency response function that relates the concentration change of the component 2 at the column outlet with the inlet concentration change
$G_n(x,\omega_1,\omega_2,\ldots,\omega_n)$	n-th order frequency response function that relates the concentration change of the component 1 at distance x from the column inlet with the inlet concentration change
$G_n^*(\omega_1,\omega_2,\ldots,\omega_n)$	n-th order frequency response function that relates the concentration change of the component 1 at the column outlet with the inlet concentration change
L	Column length, cm
N_{tp}	Number of theoretical plates
q	Dimensionless concentration in the solid phase
Q	Concentration in the solid phase, g/l
Q_s	Steady-state concentration in the solid phase, g/l
Q_0	Saturation capacity (parameter of the adsorption isotherm), g/l
t	Dimensionless time
$u(\tau)$	Input function
υ	Interstitial fluid velocity, cm/s
x	Dimensionless space coordinate
$y(\tau)$	Output function
z	Space coordinate, cm
ε	Total column porosity
τ	Time, s
ω	Dimensionless frequency
ω^*	Frequency, rad/s

1 Introduction

In the last few decades, the frequency response (FR) has been used as a method for process dynamics investigation and model identification of adsorption systems. Due to some advantages in comparison to other classical methods, the FR method is used to study adsorption, not only theoretically, but also experimentally (Boniface and Ruthven 1985; Grzegorczyk and Carta 1997; Naphtali and Polinski 1963; Park et al. 1998a, 1998b; Rees and Song 2000; Sward and LeVan 2003; Wang et al. 2003). Although most adsorption systems are nonlinear, in almost all these investigations system linearity is assumed. In the last couple of years adsorption systems have been studied theoretically using the nonlinear FR method, which enables reliable discrimination between kinetic mechanisms and estimation of kinetic and equilibrium parameters (Petkovska 2005; Petkovska and Do 2000; Petkovska and Petkovska 2003). This nonlinear method is based on a replacement of a nonlinear model of a system with an infinite series of higher order frequency response functions (FRFs) using the Volterra series and generalized Fourier transform (Weiner and Spina 1980).

The first application of the FR method in measurements of binary mixtures is done by Yasuda and co-workers who analyzed mixtures of methane, helium and krypton in zeolites (Yasuda et al. 1986). Sun with associates studied theoretically FR behavior of multiple sorbates diffusion in adsorbents (Sun et al. 1994). Park and co-workers analyzed the FR of a continuous-flow adsorber with periodic modulation of the inlet flow-rate in order to measure multicomponent diffusion kinetics in porous media (Park et al. 2000). Wang and LeVan used the pressure-swing FR method to investigate mixture diffusion in nanoporous adsorbents theoretically and experimentally (Wang and LeVan 2005a, 2005b). It has been shown that the FR method owing to its high sensitivity offers a potential to determine adsorption rates not only for pure components, but also for mixtures.

Recently the nonlinear FR method for determination of single solute adsorption isotherms based on the analysis of the nonlinear FR of a chromatographic column using the concept of the higher order FRFs is developed by Petkovska and Seidel-Morgenstern (Petkovska and Seidel-Morgenstern 2005). Using this method first three local isotherm derivatives at a certain steady-state concentration are estimated from the low frequency asymptotic behavior of the corresponding FRFs and their derivatives. Simulations of the FR of a chromatographic column have shown that the nonlinear FR method can be applied for an accurate estimation of adsorption isotherms with complex shape, e.g. isotherms possessing an inflection point (Ilić et al. 2007b). Its experimental realization is possible using a standard gradient HPLC unit and perturbing the inlet concentration in a nearly sine waveform around chosen steady-state concentrations (Ilić et al. 2007c). The nonlinear FR method for estimation of adsorption isotherms differs from other classical dynamic methods. It analyzes concentration changes over time in the frequency domain. Contrary to the most classical methods, which are based on calculation of the loading for certain concentration in the liquid phase, this method gives the first three local isotherm derivatives at certain steady-state concentration. In this way more information about isotherm shape is obtained in comparison to other methods for estimation of adsorption isotherms.

A large number of experimental methods is available for estimation of single solute adsorption isotherms as well as competitive isotherms (Seidel-Morgenstern 2004). Since it is very difficult to determine competitive adsorption isotherms experimentally, they are often derived from the single solute isotherms of the compounds involved (Guiochon et al. 1994; Ruthven 1984). It can happen that competitive isotherm exhibit quite different behavior than it is predicted by a proposed model derived from the theory, because the conditions are no more ideal as it is assumed in derivation of these models (Gritti and Guiochon 2003). This is usually the case in the higher concentration range, in which most of the separations in the preparative chromatography are carried out. In the case of multicomponent mixtures, the competition between the different components present in the mixture for interaction with the stationary phase causes an additional complexity. Molecules of different compounds compete for access to the limited number of adsorption sites, whereby the more strongly adsorbed ones tend to exclude the others. For this reason, the amount of one component adsorbed at equilibrium is no longer a function of only the concentration of this component, but also of the concentrations of all other components of the mixture that can be adsorbed on the stationary phase. In order to quantify these complex relations the competitive isotherms should be estimated experimentally in the whole concentration range that is of interest for some process.

Since the nonlinear FR method appears to be convenient for estimation of single solute adsorption isotherms with complex shapes (Ilić et al. 2007c), an extension of this method for application to binary mixtures seems to be a promising task. In this paper the FRFs up to the third order for the case when two compounds are adsorbed in a chromatographic column, are derived theoretically using the same approach as for a single adsorbing compound (Petkovska and Seidel-Morgenstern 2005). The FRFs corresponding to both components and different inlet concentration changes are derived. They are calculated numerically for different steady-state concentrations and relative compositions of the mixture and afterwards analyzed. The goal was to find correlations between the derived FRFs and coefficients of competitive adsorption isotherms, so that these functions can be later on used for estimation of competitive isotherms.

2 Theory

2.1 Frequency response of a nonlinear system

The FR represents a quasi-stationary response of a system to a periodic change of an input. All information about a linear single-input-single-output system is encoded in its FRF $H(\omega)$, because the FR of a linear system is a periodic function of the same frequency as the input function only having the different amplitude and being phase shifted in comparison to the input one. The FR of a nonlinear system comprises a non-periodic term and an indefinite number of terms corresponding to higher harmonics, which are due to the frequency domain energy transfer in nonlinear systems from high frequency modes to modes at other frequencies (Lang and Billings 2005). A convenient tool for analysis of the nonlinear FR is the concept of higher order FRFs based on the Volterra series and generalized Fourier transform (Weiner and Spina 1980). The functional form representation of input-output relationship through Volterra series provides a structured mathematical platform to study the behavior of nonlinear systems. The response of a weakly nonlinear system with polynomial nonlinearities, to an arbitrary input can be expressed in the form of the Volterra series as (Weiner and Spina 1980):

$$y(\tau) = y_1(\tau) + y_2(\tau) + y_3(\tau) + \cdots = \sum_{n=1}^{\infty} y_n(\tau) \tag{1}$$

where n-th element of the series $y_n(\tau)$ is defined as the impulse response function of the n-th order. The corresponding n-th order FRF $H_n(\omega_1, \omega_2, \ldots, \omega_n)$ is obtained by applying the multidimensional Fourier transform to $y_n(\tau)$. The general form of the output is the same whether the single-input or multi-input case is considered. The difference is in the definition of $y_n(\tau)$, which is for the single-input case expressed in terms of single Volterra elements, while for the multi-input case several direct and cross Volterra elements are required. Using the concept of higher order FRFs the nonlinear model of a system is replaced by series of functions of the first, second, ... order. More about the FR of a nonlinear systems and the concept of higher order FRFs can be found elsewhere (Rugh 1981; Weiner and Spina 1980; Worden and Tomlinson 2001).

A chromatographic column as a weakly nonlinear system can be analyzed using this concept. In case of the adsorption of a binary mixture that is considered here, in the most general case it is possible to change concentrations of both compounds at the inlet of a chromatographic column independently. A general block diagram, illustrating connections between the input (u) and output (y) using the higher order FRFs, for two-input-two-output nonlinear system is given in Fig. 1. For such a case it is necessary to define three series of FRFs: two series relating the each output to each input and one series relating the each output to both inputs.

For practical realization and application of the method that will be described later, the periodical simultaneous change of the inlet concentration of each compound with different amplitude and frequency would be a quite formidable task. Therefore, certain assumptions are made that simplify the problem. Only the case when the concentration of both compounds changes in the same way, i.e. with

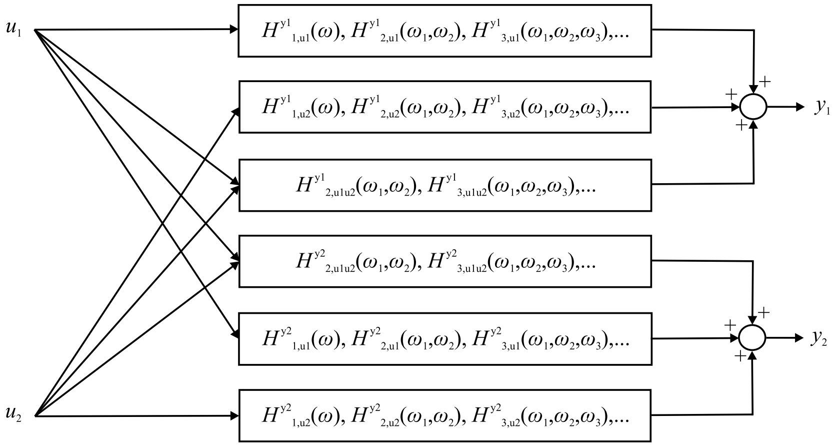


Fig. 1 Block diagram illustrating behavior of two-input-two-output nonlinear systems

the same amplitude and frequency, is considered. This allows consideration of the investigated system as a single-input-two-output system, although the different series of the FRFs corresponding to various inlet concentration changes (concentration change of only one compound keeping the other constant and concentration change of both compounds keeping their ratio constant) need to be calculated to fully describe of the analyzed nonlinear system.

Since further only the response of a nonlinear system to single-input will be considered, equations given below correspond to this case. For a single harmonic input excitation of magnitude A given as:

$$u(\tau) = A\cos(\omega^*\tau) = \frac{A}{2}e^{j\omega^*\tau} + \frac{A}{2}e^{-j\omega^*\tau} \tag{2}$$

the response of a nonlinear system can be written in the following form:

$$\begin{aligned} y &= y_{DC} + y_I + y_{II} + y_{III} + \cdots \\ &= y_{DC} + \sum_{i=I,n=1}^{\infty} B_i\cos(n\omega^*\tau + \varphi_i). \end{aligned} \tag{3}$$

The response component at the forcing frequency, i.e. corresponding to the first harmonic y_I is actually an infinite sum of different terms corresponding to this harmonic:

$$\begin{aligned} y_I &= B_I\cos(\omega^*\tau + \varphi_I) \\ &= \frac{A}{2}H_1(\omega^*)e^{j\omega^*\tau} \\ &\quad + 3\left(\frac{A}{2}\right)^3 H_3(\omega^*, \omega^*, -\omega^*)e^{j\omega^*\tau} \\ &\quad + 10\left(\frac{A}{2}\right)^5 H_5(\omega^*, \omega^*, \omega^*, -\omega^*, -\omega^*)e^{j\omega^*\tau} \\ &\quad + \mathit{higher\ order\ terms} \\ &\quad + \mathit{complex\ conjugate\ terms}. \end{aligned} \tag{4}$$

Similar, the component in the response y_{II} that corresponds to the second harmonic is:

$$\begin{aligned} y_{II} &= B_{II}\cos(2\omega^*\tau + \varphi_{II}) \\ &= \left(\frac{A}{2}\right)^2 H_2(\omega^*, \omega^*)e^{2j\omega^*\tau} \\ &\quad + 4\left(\frac{A}{2}\right)^4 H_4(\omega^*, \omega^*, \omega^*, -\omega^*)e^{2j\omega^*\tau} \\ &\quad + 15\left(\frac{A}{2}\right)^6 H_6(\omega^*, \omega^*, \omega^*, \omega^*, -\omega^*, -\omega^*)e^{2j\omega^*\tau} \\ &\quad + \mathit{higher\ order\ terms} \\ &\quad + \mathit{complex\ conjugate\ terms}. \end{aligned} \tag{5}$$

And the one y_{III} corresponding to the third harmonic is:

$$\begin{aligned} y_{III} &= B_{III}\cos(3\omega^*\tau + \varphi_{III}) \\ &= \left(\frac{A}{2}\right)^3 H_3(\omega^*, \omega^*, \omega^*)e^{3j\omega^*\tau} + 5\left(\frac{A}{2}\right)^5 \\ &\quad \times H_5(\omega^*, \omega^*, \omega^*, \omega^*, -\omega^*)e^{3j\omega^*\tau} \\ &\quad + \mathit{higher\ order\ terms} \\ &\quad + \mathit{complex\ conjugate\ terms}. \end{aligned} \tag{6}$$

The stronger the nonlinearities are, the more functions are needed for an accurate description of a nonlinear system behavior. However for a wide class of nonlinear systems, most of the dominant effects are contained in the FRFs up to the third order, which are often sufficient to characterize the system (Weiner and Spina 1980). Furthermore, for relatively small input amplitudes only the first terms in (4–6) are significant and the second and higher terms can be neglected.

2.2 Equilibrium-dispersive model for a multi-component system

One of the most often used models for description of the concentration profiles in the liquid chromatography is the equilibrium-dispersive model. For solute i in a N component mixture, it is given by the following equation (Guiochon et al. 1994):

$$\frac{\partial C_i}{\partial \tau}+\frac{1-\varepsilon}{\varepsilon}\frac{\partial Q_i}{\partial \tau}+\upsilon\frac{\partial C_i}{\partial z}=D_{app}\frac{\partial^2 C_i}{\partial z^2},\quad i=1,2,\ldots,N \tag{7}$$

where C is the concentration in the liquid phase, Q the concentration in the solid phase, τ and z are the time and space coordinates, respectively, ε is the total column porosity, υ the linear velocity and D_{app} the apparent dispersion coefficient, which is related to the number of theoretical plates. In this model it is assumed that all nonequilibrium contributions can be lumped into the apparent dispersion coefficient. Another assumption is that the two phases present in the column are constantly in the equilibrium, which is expressed by the following general form of an adsorption isotherm for each component:

$$Q_i=Q_i(C_1,C_2,\ldots,C_N),\quad i=1,2,\ldots,N. \tag{8}$$

As it can be seen from (8), the concentration of one component in the solid phase depends on the concentrations of all components present in the liquid phase.

In order to solve (7) it is necessary to specify initial and boundary conditions. The initial conditions for the preloaded column may be written as:

$$\begin{aligned}&\tau\le 0:\quad C_i(z)=C_{i,in}(z)=C_{si}=C_{si,in};\\&Q_i(z)=Q_{si}=Q_i(C_{s1},C_{s2},\ldots,C_{sN}),\\&\quad i=1,2,\ldots,N\end{aligned} \tag{9}$$

where the subscript *in* denotes the values at the column inlet and the subscript s the steady-state values. In case that the column is not preloaded, the concentrations in the liquid and solid phases are equal to zero. The Danckwert's boundary conditions (Dankwerts 1953) given by (10) are usually used for solving the equilibrium-dispersive model.

$$\begin{aligned}&z=0:\quad C_i(0,\tau)=C_{i,in}(\tau)+D_{app}\left.\frac{\partial C_i}{\partial z}\right|_{z=0};\\&z=L:\quad \left.\frac{\partial C_i}{\partial z}\right|_{z=1}=0,\quad i=1,2,\ldots,N.\end{aligned} \tag{10}$$

In the single component adsorption case it has been shown that, although the equilibrium-dispersive model assumes that the concentration in the solid phase is in equilibrium with the concentration in the liquid phase, it gives the same results in the low frequency region as a model considering finite transfer rates between the liquid and solid phase (Petkovska and Seidel-Morgenstern 2005). This region is of interest for estimation of isotherm parameters. For this reason, the FRFs for the adsorption of a binary mixture are derived only for the equilibrium-dispersive model.

For further analysis, it is more convenient to use the above given equations (7–10) in a dimensionless form, which is obtained by an appropriate transformation. Since a binary mixture is analyzed in this paper, these equations will be given for this considered case. The equilibrium-dispersive model (7) may be written in the following dimensionless form:

$$\frac{\partial c_i}{\partial t}+f_i\frac{\partial q_i}{\partial t}+\frac{\partial c_i}{\partial x}=\frac{1}{2N_{tp}}\cdot\frac{\partial^2 c_i}{\partial x^2},\quad i=1,2 \tag{11}$$

where c and q are the dimensionless concentrations in the liquid and solid phases, respectively, defined as relative deviations from the corresponding steady-state concentrations (12), t and x are the dimensionless time and space coordinates (13), respectively; f is the dimensionless factor and N_{tp} the number of theoretical plates, both defined by (14).

$$c_i=\frac{C_i-C_{si}}{C_{si}},\qquad q_i=\frac{Q_i-Q_{si}}{Q_{si}}, \tag{12}$$

$$t=\tau\frac{\upsilon}{L},\qquad x=\frac{z}{L}, \tag{13}$$

$$f_i=\frac{1-\varepsilon}{\varepsilon}\cdot\frac{Q_{si}}{C_{si}},\qquad N_{tp}=\frac{\upsilon L}{2D_{app}}. \tag{14}$$

The initial conditions in a dimensionless form are:

$$t\le 0:\quad c_i(x)=c_{i,in}(x)=q_i(x)=0,\quad i=1,2 \tag{15}$$

where $c_{i,in}$ is the dimensionless inlet concentration in the liquid phase defined as:

$$c_{i,in}=\frac{C_{i,in}-C_{si}}{C_{si}}. \tag{16}$$

The corresponding dimensionless form of the Danckwert's boundary conditions is:

$$\begin{aligned}&x=0:\quad c_i(0,t)=c_{i,in}(t)+\frac{1}{2N_{tp}}\cdot\left.\frac{\partial c_i}{\partial x}\right|_{x=0};\\&x=1:\quad \left.\frac{\partial c_i}{\partial x}\right|_{x=1}=0,\quad i=1,2.\end{aligned} \tag{17}$$

The competitive adsorption isotherm in a dimensionless form describes the local equilibrium at certain steady-state. It is defined as Taylor series expanded around steady-state concentrations of both compounds (C_{s1} and C_{s2}):

$$\begin{aligned}q_i&=\tilde{a}_{i1}c_1+\tilde{a}_{i2}c_2+\tilde{b}_{i1}c_1^2+\tilde{b}_{i2}c_2^2+\tilde{b}_{i3}c_1c_2+\tilde{c}_{i1}c_1^3\\&\quad+\tilde{c}_{i2}c_2^3+\tilde{c}_{i3}c_1^2c_2+\tilde{c}_{i4}c_1c_2^2+\cdots,\quad i=1,2\end{aligned} \tag{18}$$

whereby the coefficients of the dimensionless competitive isotherm are defined as local partial derivatives of the adsorption isotherm in the dimensional form for a chosen steady-state:

$$\tilde{a}_{i1} = \left.\frac{\partial Q_i}{\partial C_1}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1}}{Q_{si}};$$

$$\tilde{a}_{i2} = \left.\frac{\partial Q_i}{\partial C_2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s2}}{Q_{si}}, \quad i = 1, 2; \tag{19a}$$

$$\tilde{b}_{i1} = \frac{1}{2} \cdot \left.\frac{\partial^2 Q_i}{\partial C_1^2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1}^2}{Q_{si}};$$

$$\tilde{b}_{i2} = \frac{1}{2} \cdot \left.\frac{\partial^2 Q_i}{\partial C_2^2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s2}^2}{Q_{si}}, \quad i = 1, 2; \tag{19b}$$

$$\tilde{c}_{i1} = \frac{1}{6} \cdot \left.\frac{\partial^3 Q_i}{\partial C_1^3}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1}^3}{Q_{si}};$$

$$\tilde{c}_{i2} = \frac{1}{6} \cdot \left.\frac{\partial^3 Q_i}{\partial C_2^3}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s2}^3}{Q_{si}}, \quad i = 1, 2. \tag{19c}$$

The isotherm coefficients that correspond to cross terms ($c_1c_2, c_1^2c_2, c_1c_2^2$) are defined as mixed partial derivatives:

$$\tilde{b}_{i3} = \left.\frac{\partial^2 Q_i}{\partial C_1 \partial C_2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1} \cdot C_{s2}}{Q_{si}}, \quad i = 1, 2; \tag{19d}$$

$$\tilde{c}_{i3} = \frac{1}{2} \cdot \left.\frac{\partial^3 Q_i}{\partial C_1^2 \partial C_2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1}^2 \cdot C_{s2}}{Q_{si}};$$

$$\tilde{c}_{i4} = \frac{1}{2} \cdot \left.\frac{\partial^3 Q_i}{\partial C_1 \partial C_2^2}\right|_{C_{s1},C_{s2}} \cdot \frac{C_{s1} \cdot C_{s2}^2}{Q_{si}}, \quad i = 1, 2; \tag{19e}$$

From (18–19e) it can be noticed that if it is possible to extract all coefficients of the isotherm in the dimensionless form, then a lot of valuable information about isotherm and its shape corresponding to the chosen steady-state concentration can be obtained.

3 Derivation of the first, second and third order FRFs

The derivation of the FRFs up to the third order is performed for the dimensionless frequency defined as:

$$\omega = \omega^* \frac{L}{\upsilon} \tag{20}$$

where ω^* is the frequency in rad/s. In order to avoid an overloading of the main body of the paper with rather complex and cumbersome equations, a detailed procedure for derivation of the FRFs of both components up to the third order is given in the Appendix. Below will be described only the main steps of this procedure.

3.1 Definition of the inlet concentration change

As it is mentioned before, although two components are present in the inlet mixture the analyzed system is considered as a single-input system. However, there are still different possibilities for the periodical concentration change of two compounds at the inlet of a column. In the case that the concentration of only one of two components (component 1 or component 2) changes periodically at the inlet, while the concentration of the other component is constant, the inlet concentration change can be written as:

$$c_{i,in}(t) = A\cos(\omega t) = \frac{A}{2}(e^{j\omega t} + e^{-j\omega t}); \qquad c_{k,in} = 0, \quad i, k = 1, 2; \quad i \neq k. \tag{21}$$

The FRFs calculated for this type of the inlet concentration change will be denoted below by C1 in the subscript when the concentration of the component 1 is periodically changed and by C2 when the concentration of the component 2 is changed. If the concentration of both components changes periodically at the inlet keeping their ratio constant, then the inlet concentration change is given as:

$$c_{i,in}(t) = A\cos(\omega t) = \frac{A}{2}(e^{j\omega t} + e^{-j\omega t}), \quad i = 1, 2. \tag{22}$$

Here it should be noticed that due to the identical definition of the inlet concentration change for both compounds it is possible to describe also this case by only one input function which is the total concentration change. The FRFs calculated for this case will be denoted below by C1&C2 in the subscript.

3.2 Representation of the liquid phase concentration in the Volterra series form

The dimensionless concentrations in the liquid phase at distance x from the column inlet ($c_i(x,t)$) in the Voltera series form are expressed by (23). This equation comprises only terms required for derivation of the FRFs up to the third order.

$$\begin{aligned} c_i(x,t) = {} & \frac{A}{2} H_1^{(i)}(x,\omega)e^{j\omega t} + \frac{A}{2} H_1^{(i)}(x,-\omega)e^{-j\omega t} \\ & + \left(\frac{A}{2}\right)^2 H_2^{(i)}(x,\omega,\omega)e^{2j\omega t} \\ & + 2\left(\frac{A}{2}\right)^2 H_2^{(i)}(x,\omega,-\omega)e^{0} \\ & + \left(\frac{A}{2}\right)^2 H_2^{(i)}(x,-\omega,-\omega)e^{-2j\omega t} \\ & + \left(\frac{A}{2}\right)^3 H_3^{(i)}(x,\omega,\omega,\omega)e^{3j\omega t} \end{aligned}$$

$$+3\left(\frac{A}{2}\right)^3 H_3^{(i)}(x,\omega,\omega,-\omega)e^{j\omega t}$$

$$+3\left(\frac{A}{2}\right)^3 H_3^{(i)}(x,\omega,-\omega,-\omega)e^{-j\omega t}$$

$$+\left(\frac{A}{2}\right)^3 H_3^{(i)}(x,-\omega,-\omega,-\omega)e^{-3j\omega t}+\cdots,$$

$$i=1,2;\qquad G=H^{(1)};\qquad F=H^{(2)}. \tag{23}$$

The H-functions represent actually two different functions. For the sake of the manuscript clarity they are denoted by different letters for different i, i.e. different compound. For $i=1$ they are denoted by G-functions which relate the concentration of the component 1 in the liquid phase at distance x from the column inlet to the inlet concentration change and for $i=2$ by the F-functions which relate the concentration of the component 2 to the inlet concentration change. The functions which relate the outlet concentration to the inlet concentration change will be denoted below by an asterisk ($*$) in the superscript.

3.3 Representation of the solid phase concentration in the Volterra series form

In order to obtain the dimensionless concentrations in the solid phase at distance x from the column inlet in the Volterra series form, it is necessary to introduce (23) into (18). The obtained rather cumbersome expression that considers only terms which are important for derivation of the first, second and third order FRFs is given in the Appendix.

3.4 Substitution of the concentrations defined in the previous steps into the model and boundary conditions

As a result of substitution of the inlet concentration change (21) or (22), liquid phase concentration (23) and solid phase concentration (28) into (11) and (17), the model and boundary conditions are expressed in the corresponding Volterra series form. The obtained equations are omitted for the sake of the paper brevity.

3.5 Application of the harmonic probing method

This method is applied to the equations from the previous step. It is based on collecting terms with $(A/2)e^{j\omega t}$, $(A/2)^2e^{2j\omega t}$ and $(A/2)^3e^{3j\omega t}$ and equating them to zero. The resulting equations define the first, second and third order FRFs, whereby time as independent variable is replaced by frequency and the liquid and solid phase concentrations as dependent variables by sets of the corresponding FRFs.

3.6 Solution of the equations from the steps 3.4 and 3.5

In order to obtain explicit expressions for each FRF of interest, the equations obtained in the previous step need to be solved. It should be emphasized that the solution procedure is recursive. First should be solved equation corresponding to the first order FRF, then to the second order function and afterwards to the third order one. More about the procedure for derivation of the higher order FRFs of adsorption systems can be found in (Petkovska 2005). The other higher order FRFs can be obtained using the same procedure and considering higher terms that correspond to these functions.

Below will be presented some of the results obtained from the analysis of the derived FRFs corresponding to both components and different initial conditions, e.g. steady-state concentrations and relative mixture compositions.

4 Analysis of the derived FRFs for the adsorption of a binary mixture

Due to the complexity of the analytical expressions of the FRFs, their direct analysis would be quite a formidable task. Therefore, they are at first calculated here numerically for certain number of points (frequencies) and a concrete system and then analyzed. The adsorption of ethyl benzoate and 4-tert-butylphenol as adsorbates on the octadecyl silica as adsorbent using methanol and water as a solvent is used for this case study. The single solute adsorption isotherms of these compounds for the studied conditions were found to be the BET and Langmuir isotherms, respectively (Gritti and Guiochon 2003). The competitive isotherms for these compounds were derived from the ideal adsorbed solution theory (Guiochon et al. 1994). In that way the following equations for the binary Langmuir-BET competitive isotherms were obtained (Gritti and Guiochon 2003):

$$Q_{EB}=Q_{0,EB}\frac{(b_{S,EB}+b_{L,EB}b_{S,TBP}C_{TBP})\cdot C_{EB}}{(1-b_{L,EB}C_{EB})\cdot(1-b_{L,EB}C_{EB}+b_{S,EB}C_{EB}+b_{S,TBP}C_{TBP})}, \tag{24a}$$

$$Q_{TBP}=Q_{0,TBP}\frac{(b_{S,TBP}-b_{L,EB}b_{S,TBP}C_{EB})\cdot C_{TBP}}{(1-b_{L,EB}C_{EB})\cdot(1-b_{L,EB}C_{EB}+b_{S,EB}C_{EB}+b_{S,TBP}C_{TBP})} \tag{24b}$$

where the subscript EB denotes ethyl benzoate as the component 1 in further notation and the subscript TBP denotes 4-tert-butylphenol as the component 2; Q_0 is the saturation capacity, b_S is the parameter that defines surface adsorption-desorption over the free surface of the adsorbent and b_L surface adsorption-desorption over a layer of adsorbate molecules.

The values of the adsorption isotherm coefficients used for the calculations done in this work correspond to the systems investigated by Gritti and Guiochon (2003) and they are summarized in Table 1. The other parameters used

Table 1 Coefficients of the competitive adsorption isotherms used for calculation of the FRFs (Gritti and Guiochon 2003)

$Q_{0,\mathrm{EB}}$ [g/l]	237.7
$b_{S,\mathrm{EB}}$ [l/g]	0.03136
$b_{L,\mathrm{EB}}$ [l/g]	0.0111
$Q_{0,\mathrm{TBP}}$ [g/l]	164.0
$b_{S,\mathrm{TBP}}$ [l/g]	0.05613

for the calculation correspond also to the system and experimental conditions from the same reference work. They are: a flow rate of 1 ml/min, a total column porosity of 0.577 and 25 cm long column with an internal diameter of 4.6 mm. The FRFs are calculated for different inlet concentration changes, steady-state concentrations and relative mixture compositions for 1000 theoretical plates and in the frequency range from 10^{-5} to 1 rad/s.

4.1 Different inlet concentration changes

Three different possibilities of the inlet concentration change of ethyl benzoate and 4-tert-butylphenol are considered. They correspond to different initial conditions used for derivation of the FRFs of a chromatographic column for the adsorption of a binary mixture, which are mentioned in the previous section. The amplitudes and phases of the first, second and third order FRFs, which relate the outlet concentration change of ethyl benzoate to different inlet concentration changes, vs. frequency are given in Figs. 2–4. Figures 5–7 show the amplitudes and phases of the FRFs, which relate the outlet concentration change of 4-tert-butylphenol to different inlet concentration changes, vs. frequency.

The shown FRFs correspond to the steady-state concentration of 5 g/l for each component. As it can be seen in Fig. 2 the amplitudes and phases of the first order FRFs $G^*_{1,C1}(\omega)$ and $G^*_{1,C1\&C2}(\omega)$ have the same shape. Their amplitudes tend to 1 for low frequencies and to 0 for high frequencies and the phases tend to 0 for low frequencies and to $-\infty$ for high frequencies. On the other hand, the amplitude and phase of first order FRF $G^*_{1,C2}(\omega)$ differ from the two previously mentioned functions only in the low frequency range, whereby the amplitude tends to 0 and the phase to $+\pi/2$. The first order FRF $F^*_{1,C1\&C2}(\omega)$ shows the same behavior as $G^*_{1,C1\&C2}(\omega)$(compare Figs. 2 and 5). The amplitude of $F^*_{1,C2}(\omega)$ tends to 1 for low frequencies and to 0 for high frequencies, while the phase tends to 0 for low frequencies and to $-\infty$ for high frequencies. The behavior of $F^*_{1,C1}(\omega)$ is the same as the behavior of $G^*_{1,C2}(\omega)$ (compare Figs. 2 and 5). The second ($G^*_2(\omega,\omega)$ and $F^*_2(\omega,\omega)$) and third order FRFs ($G^*_3(\omega,\omega,\omega)$ and $F^*_3(\omega,\omega,\omega)$) have similar shapes regardless of the inlet concentration change (see Figs. 3, 4, 6 and 7). The amplitudes tend to 0 for low and high frequencies, while the phases tend to either $+\pi/2$ or $-\pi/2$ for low frequencies and to $-\infty$ for high frequencies. Also it can be noticed that the amplitudes of these functions have maximums in the frequency range from 0.01 to 0.1 rad/s. In the same frequency range a certain oscillatory behavior can be noticed. It can be partially due to the interplay of kinetics and adsorption equilibrium, but also due to the coupling of the periodic changes of the concentration of two compounds within the chromatographic column. Similar behavior has already been observed for shell-and-tube heat exchangers, when the temperature of the heating fluid is sinusoidally changed (Douglas 1972).

It has been shown in our previous work, that the FRFs of a chromatographic column for the single component adsorption corresponding to different steady-state concentrations exhibit similar behavior (Ilić et al. 2007a). The same results are obtained for the adsorption of a binary mixture. The FRFs are calculated for different steady-state concentrations of both components (1, 5, 10 and 15 g/l) and the same relative mixture composition of 1:1. For the sake of the paper brevity the corresponding figures are omitted, because they exhibit similar behavior, and only values of the low frequency asymptotes of the FRF first derivatives are summarized in Table 2. In Sect. 5 it will be explained why the products of dimensionless isotherm coefficients and factor f_i are given in the first column of the table.

The sign change, that indicates differences in the isotherm curvature, can be noticed in the value of $2\tilde{b}_{11}f_1$ between the steady-state concentrations 5 and 10 g/l and in the value of $2(\tilde{b}_{11}+\tilde{b}_{12}+\tilde{b}_{13})f_1$ between the steady-state concentrations 10 and 15 g/l. The adsorption isotherm of ethyl benzoate for the relative mixture composition of 1:1 has an inflection point at approximately 12.8 g/l. This means that existence of an inflection point can be identified from the sign change of the low frequency asymptotic value of the second order FRF, similar as for the single solute isotherm (Petkovska and Seidel-Morgenstern 2005). The concentration range in which this point occurs can be obtained from the low frequency asymptotic behavior of the phase of the second order FRF for the inlet concentration change of both components. It can be also noticed that the low frequency asymptotic values of the derivatives of some FRFs increase or decrease for higher steady-state concentrations. In some cases, these differences are even two orders of magnitude.

4.2 Different relative mixture compositions

It is well known that the increase of the concentration of one component in the mixture influences not only on the adsorbed amount of this component, but also of all other adsorbable components present in the mixture. In order to investigate effects of an increase of the ethyl benzoate concentration on the FRFs corresponding to both components,

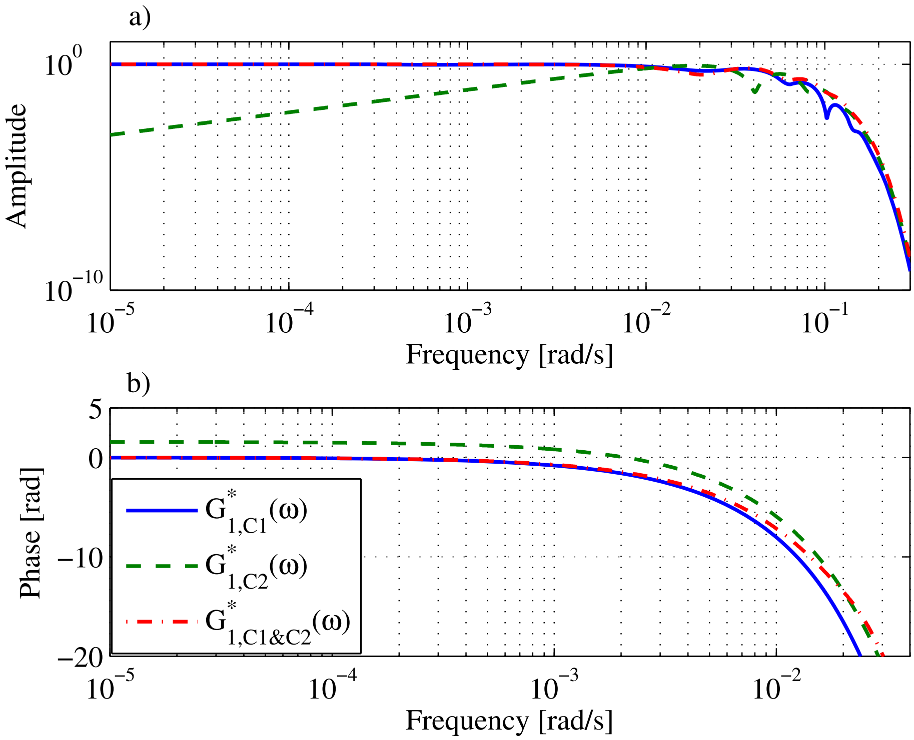


Fig. 2 Amplitude (**a**) and phase (**b**) of the first order FRF $G_1^*(\omega)$ which relates the outlet concentration change of the component 1 (ethyl benzoate) for different inlet concentration changes ($C_{s1} = C_{s2} = 5$ g/l)

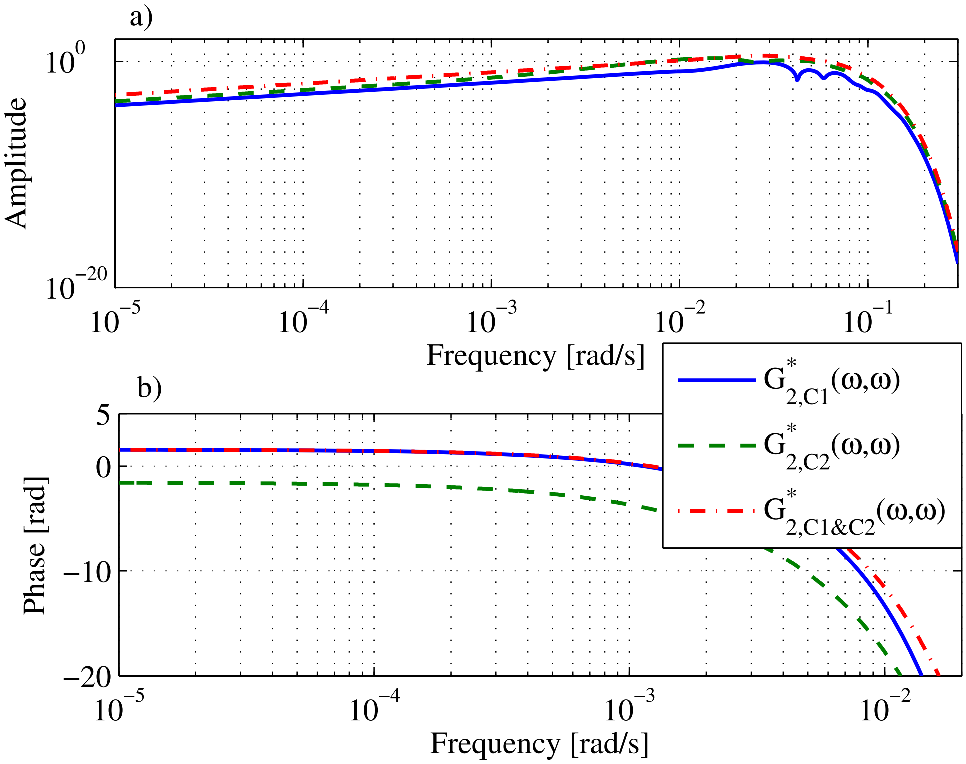


Fig. 3 Amplitude (**a**) and (**b**) phase of the second order FRF $G_2^*(\omega, \omega)$ which relates the outlet concentration change of the component 1 for different inlet concentration changes (same conditions as in Fig. 2)

these functions are calculated and compared for different relative compositions of the mixture (C_{s1}:C_{s2} = 1:1, 2:1, 5:1 and 10:1). Figures 8–10 illustrate the FRFs corresponding to ethyl benzoate which are calculated for the inlet concentration change of both components. As in the previous case the FRFs are given in the Bode plot form.

In the low frequency range, the amplitudes of the first order functions tend to 1 and their phases to 0, while in

Fig. 4 Amplitude (**a**) and phase (**b**) of the third order FRF $G_3^*(\omega, \omega, \omega)$ which relates the outlet concentration change of the component 1 for different inlet concentration changes (same conditions as in Fig. 2)

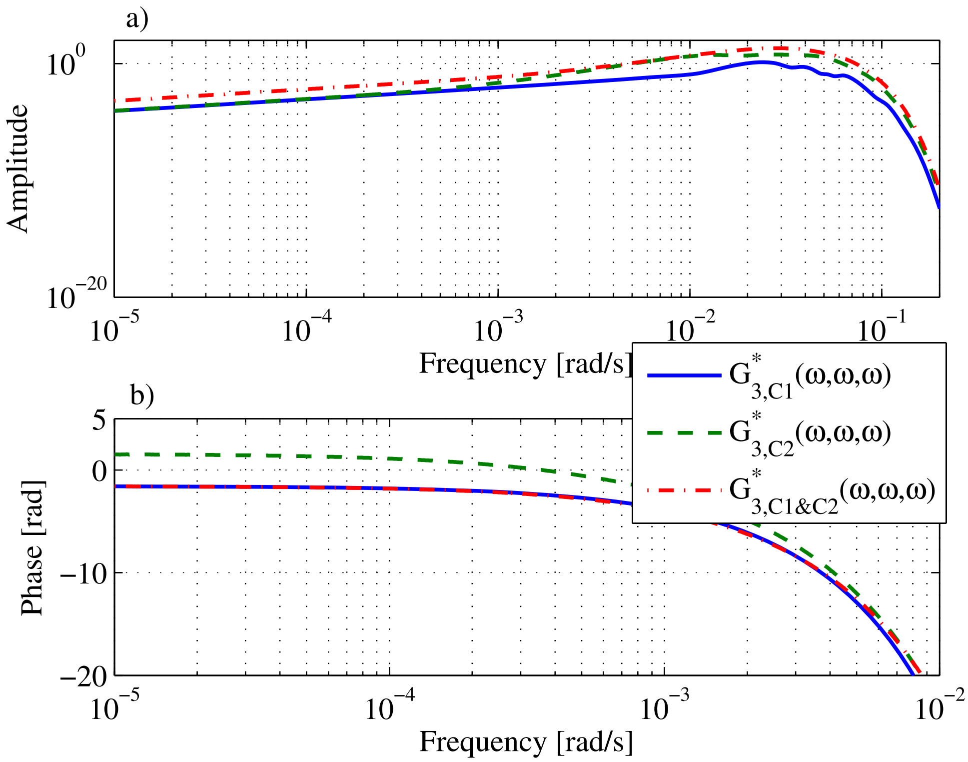
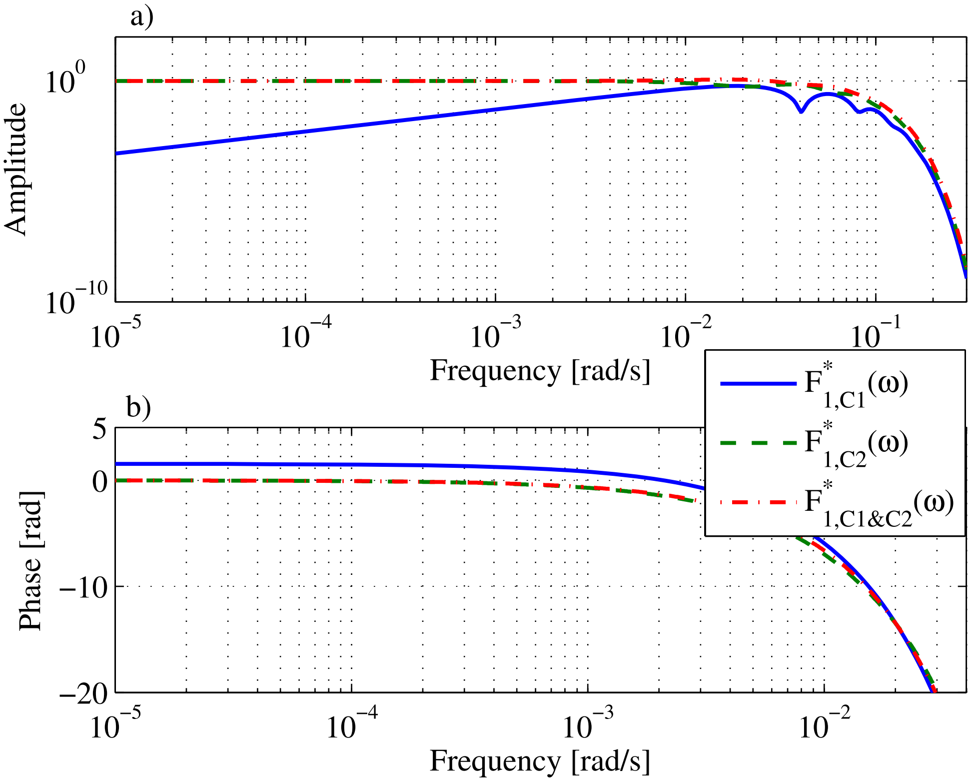


Fig. 5 Amplitude (**a**) and phase (**b**) of the first order FRF $F_1^*(\omega)$ which relates the outlet concentration change of the component 2 (4-tert-butylphenol) for different inlet concentration changes (same conditions as in Fig. 2)



the high frequency range the amplitudes tend to 0 and the phases to $-\infty$. The amplitudes have maximum in the frequency range from 0.01 to 0.1 rad/s and overshoot the low frequency asymptotic value, whereby certain differences for various mixture compositions can be noticed (see Fig. 8a). The function $G_{1,C1\&C2}^*(\omega)$ corresponding to the relative composition of 1:1 has the highest maximum value and the one corresponding to the relative composition of 10:1 does

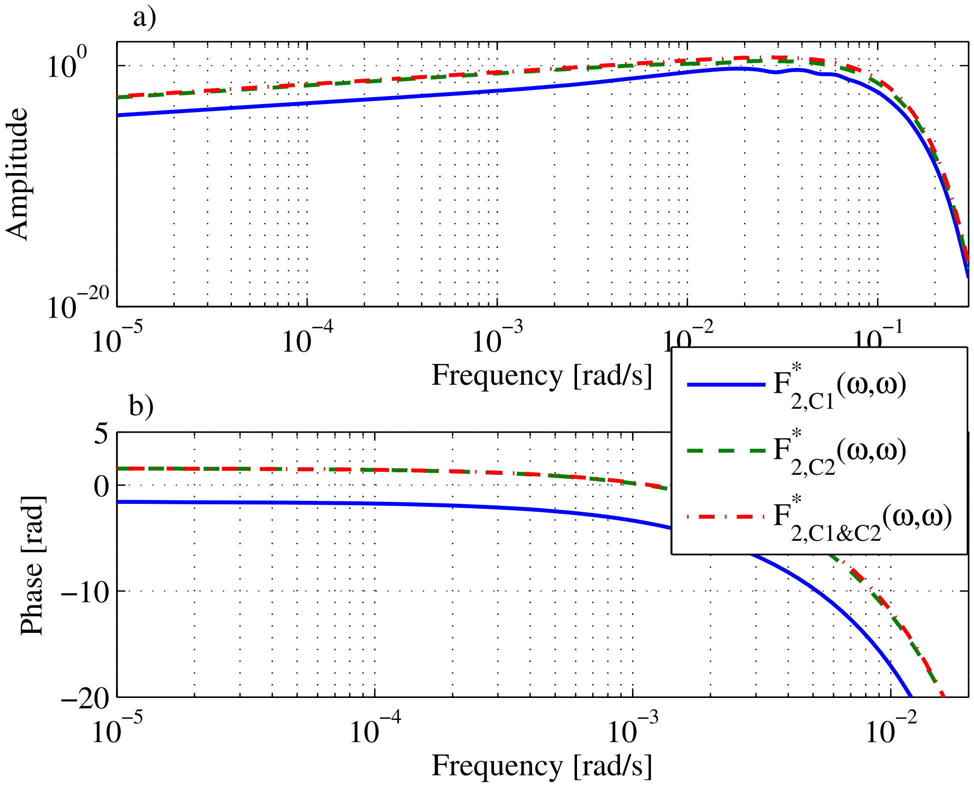


Fig. 6 Amplitude (**a**) and phase (**b**) of the second order FRF $F_2^*(\omega,\omega)$ which relates the outlet concentration change of the component 2 for different inlet concentration changes (same conditions as in Fig. 2)

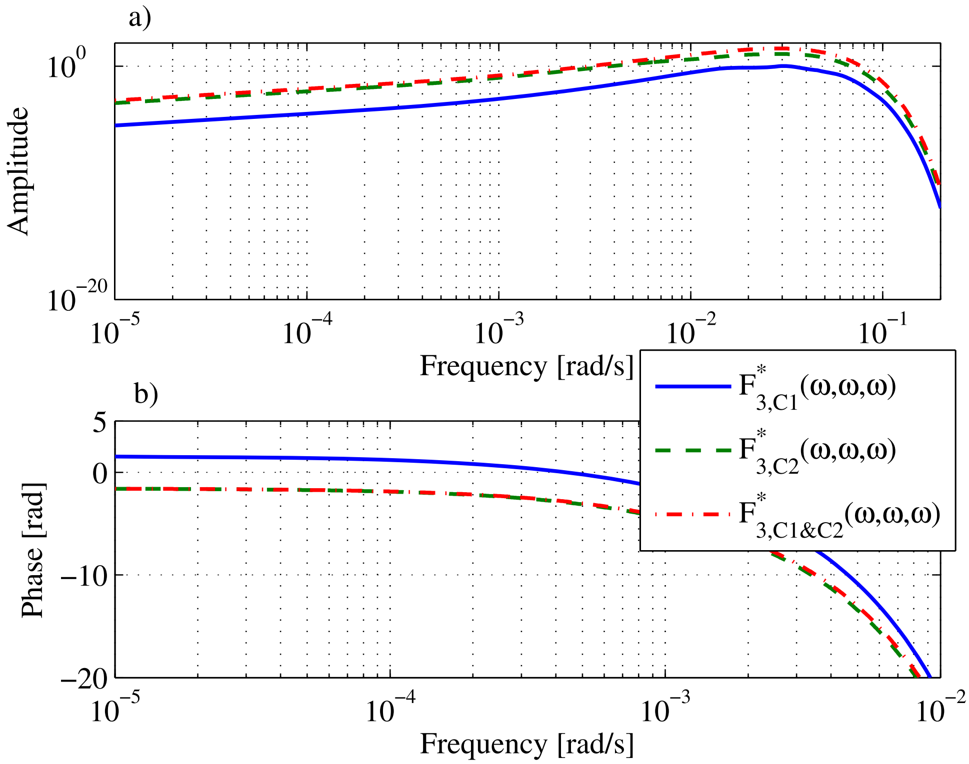


Fig. 7 Amplitude (**a**) and phase (**b**) of the third order FRF $F_3^*(\omega,\omega,\omega)$ which relates the outlet concentration change of the component 2 for different inlet concentration changes (same conditions as in Fig. 2)

not have maximum at all. The second and third order FRFs exhibit similar shapes. The amplitudes tend to 0 for low and high frequencies and have maximum, which exceeds 1 for some of the studied relative compositions of the mixture. The phases tend either to $+\pi/2(G^*_{2,C1\&C2}(\omega,\omega))$ or to $-\pi/2(G^*_{3,C1\&C2}(\omega,\omega,\omega))$ in the low frequency range

Table 2 Values of the low frequency asymptotes of the first derivatives of the FRFs corresponding to both components calculated for different steady-state concentrations and the relative composition of the mixture of 1:1

$C_{s1} = C_{s2}$ [g/l]	1	5	10	15
$1 + \tilde{a}_{11} f_1$	6.196	5.536	5.219	5.196
$\tilde{a}_{21} f_2$	−0.118	−0.358	−0.439	−0.445
$2\tilde{b}_{11} f_1$	−0.0768	−0.0923	0.204	0.712
$2\tilde{b}_{21} f_2$	4.44×10^{-3}	0.0525	0.101	0.126
$3\tilde{c}_{11} f_1$	4.17×10^{-3}	0.0607	0.185	0.418
$3\tilde{c}_{21} f_2$	-1.27×10^{-4}	-5.77×10^{-3}	−0.0174	−0.0267
$\tilde{a}_{12} f_1$	−0.171	−0.519	−0.637	−0.646
$1 + \tilde{a}_{22} f_2$	6.943	4.892	3.608	2.911
$2\tilde{b}_{12} f_1$	0.0178	0.211	0.405	0.507
$2\tilde{b}_{22} f_2$	−0.620	−1.581	−1.660	−1.500
$3\tilde{c}_{12} f_1$	-1.29×10^{-3}	−0.0642	−0.193	−0.298
$3\tilde{c}_{22} f_2$	0.0485	0.0482	0.0492	0.883
$1 + (\tilde{a}_{11} + \tilde{a}_{12}) f_1$	6.025	5.017	4.582	4.551
$1 + (\tilde{a}_{21} + \tilde{a}_{22}) f_2$	6.825	4.534	3.169	2.466
$2(\tilde{b}_{11} + \tilde{b}_{12} + \tilde{b}_{13}) f_1$	−0.388	−0.767	−0.372	0.294
$2(\tilde{b}_{21} + \tilde{b}_{22} + \tilde{b}_{23}) f_2$	−0.827	−1.953	−1.879	−1.565
$3(\tilde{c}_{11} + \tilde{c}_{12} + \tilde{c}_{13} + \tilde{c}_{14}) f_1$	0.0468	0.446	0.753	0.989
$3(\tilde{c}_{21} + \tilde{c}_{22} + \tilde{c}_{23} + \tilde{c}_{24}) f_2$	0.0880	0.810	1.220	1.254

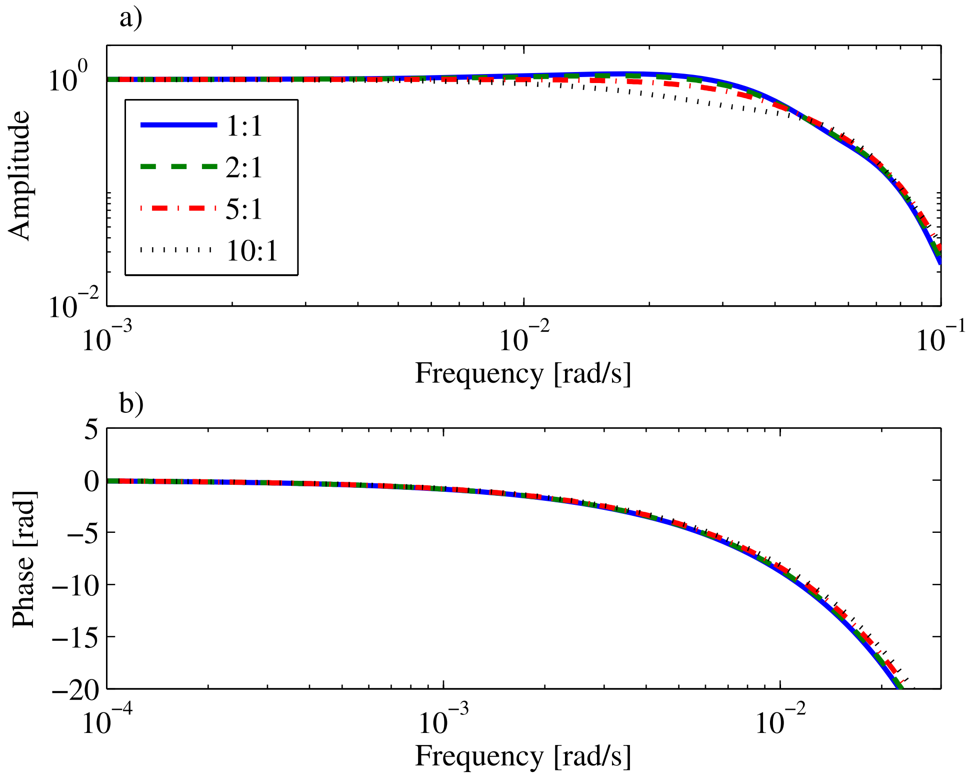


Fig. 8 Amplitude (**a**) and phase (**b**) of the first order FRF $G^*_{1,C1\&C2}(\omega)$ for different relative mixture compositions (C_{s1}:C_{s2} = 1:1, 2:1, 5:1 and 10:1)

and to $-\infty$ for higher frequencies. The oscillatory behavior in the frequency range from 0.01 to 0.1 rad/s, that has been observed in the previous analyzed cases, can also be noticed in Figs. 8–10. The functions corresponding to 4-tert-butylphenol have very similar shape and there is no need to illustrate them as well. The phases of $F^*_{2,C1\&C2}(\omega,\omega)$ and $F^*_{3,C1\&C2}(\omega,\omega,\omega)$ have the same low frequency asymptotic values as $G^*_{2,C1\&C2}(\omega,\omega)$ and $G^*_{3,C1\&C2}(\omega,\omega,\omega)$. The

Fig. 9 Amplitude (**a**) and (**b**) phase of the second order FRF $G^*_{2,C1\&C2}(\omega,\omega)$ for different relative mixture compositions (same conditions as in Fig. 8)

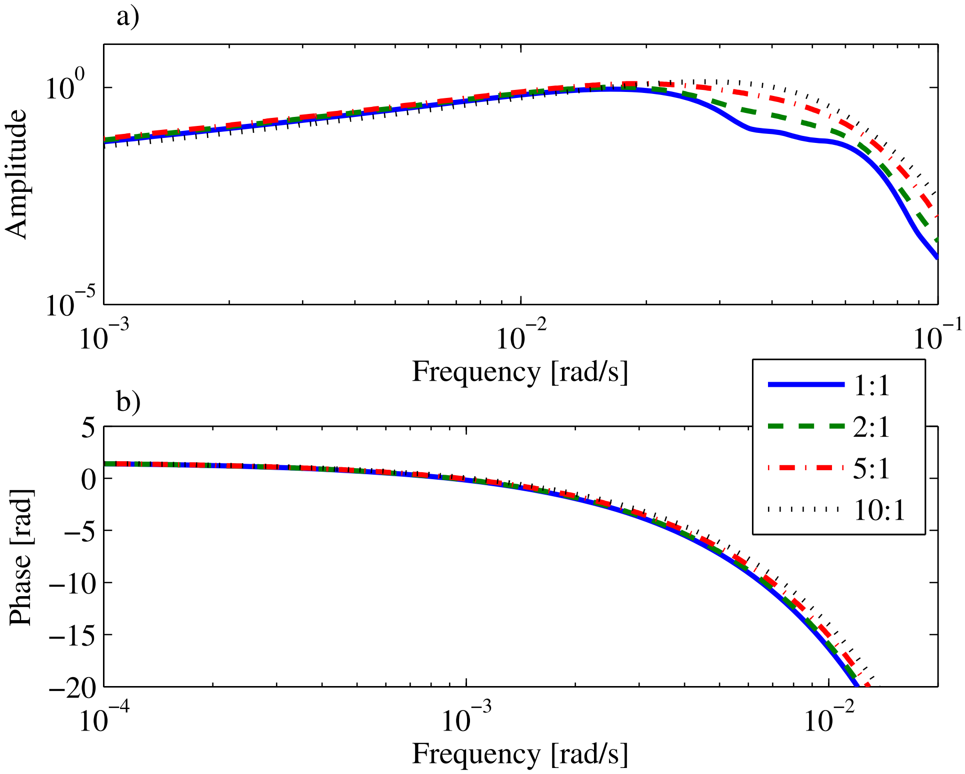
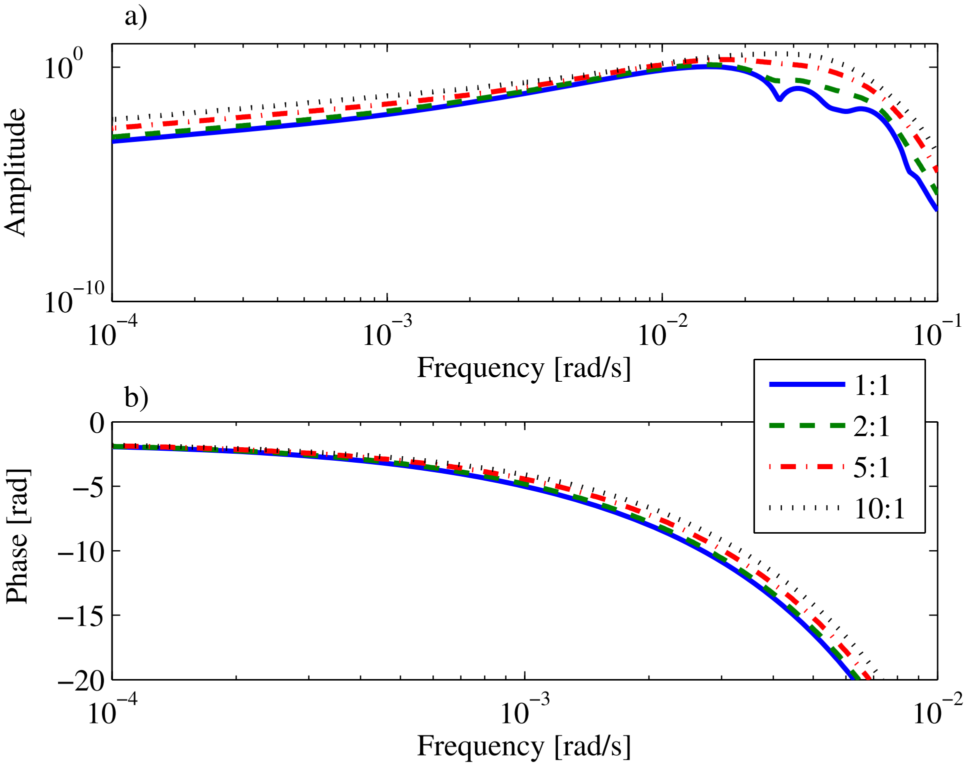


Fig. 10 Amplitude (**a**) and phase (**b**) of the third order FRF $G^*_{3,C1\&C2}(\omega,\omega,\omega)$ for different relative mixture compositions (same conditions as in Fig. 8)



only difference is for the first order function $F^*_{1,C1\&C2}(\omega)$, for which the amplitude corresponding to the relative mixture composition of 10:1 has the highest maximum value.

Table 3 comprises the low frequency asymptotic values of the derivatives of the FRFs given in Figs. 8–10 and the FRFs calculated for the inlet concentration change of only

Table 3 Values of the low frequency asymptotes of the first derivatives of the FRFs corresponding to both components calculated for different relative mixture compositions of (C_{s1}:C_{s2} = 1:1, 2:1, 5:1 and 10:1)

C_{s1}:C_{s2}	1:1	2:1	5:1	10:1
$1+\tilde{a}_{11}f_1$	6.196	6.123	5.952	5.801
$\tilde{a}_{21}f_2$	−0.118	−0.227	−0.510	−0.863
$2\tilde{b}_{11}f_1$	−0.0768	−0.137	−0.232	−0.146
$2\tilde{b}_{21}f_2$	4.44×10^{-3}	0.0168	0.0893	0.278
$3\tilde{c}_{11}f_1$	4.17×10^{-3}	0.0158	0.0863	0.297
$3\tilde{c}_{21}f_2$	-1.27×10^{-4}	-9.30×10^{-4}	−0.0117	−0.0671
$\tilde{a}_{12}f_1$	−0.171	−0.309	−0.585	−0.792
$1+\tilde{a}_{22}f_2$	6.943	6.368	5.068	3.753
$2\tilde{b}_{12}f_1$	0.0178	0.0613	0.253	0.563
$2\tilde{b}_{22}f_2$	−0.620	−1.064	−1.756	−1.954
$3\tilde{c}_{12}f_1$	-1.29×10^{-3}	-9.20×10^{-3}	−0.0808	−0.295
$3\tilde{c}_{22}f_2$	0.0485	0.158	0.568	1.040
$1+(\tilde{a}_{11}+\tilde{a}_{12})f_1$	6.025	5.959	5.804	5.676
$1+(\tilde{a}_{21}+\tilde{a}_{22})f_2$	6.825	6.611	6.037	5.259
$2(\tilde{b}_{11}+\tilde{b}_{12}+\tilde{b}_{13})f_1$	−0.388	−0.426	−0.462	−0.305
$2(\tilde{b}_{21}+\tilde{b}_{22}+\tilde{b}_{23})f_2$	−0.827	−0.989	−1.371	−1.751
$3(\tilde{c}_{11}+\tilde{c}_{12}+\tilde{c}_{13}+\tilde{c}_{14})f_1$	0.0468	0.0715	0.169	0.397
$3(\tilde{c}_{21}+\tilde{c}_{22}+\tilde{c}_{23}+\tilde{c}_{24})f_2$	0.0880	0.131	0.280	0.540

Table 4 Values of the low frequency asymptotes of the first derivatives of the FRFs corresponding to both components calculated for different relative compositions of the mixture (C_{s1}:C_{s2} = 1:1, 1:2, 1:5 and 1:10)

C_{s1}:C_{s2}	1:1	1:2	1:5	1:10
$1+\tilde{a}_{11}f_1$	6.196	6.040	5.650	5.182
$\tilde{a}_{21}f_2$	−0.118	−0.107	−0.0808	−0.0547
$2\tilde{b}_{11}f_1$	−0.0768	−0.0651	−0.0388	−0.0121
$2\tilde{b}_{21}f_2$	4.44×10^{-3}	3.82×10^{-3}	2.52×10^{-3}	1.40×10^{-3}
$3\tilde{c}_{11}f_1$	4.17×10^{-3}	3.69×10^{-3}	2.69×10^{-3}	1.83×10^{-3}
$3\tilde{c}_{21}f_2$	-1.27×10^{-4}	1.08×10^{-4}	5.81×10^{-5}	2.67×10^{-5}
$\tilde{a}_{12}f_1$	−0.171	−0.165	−0.148	−0.125
$1+\tilde{a}_{22}f_2$	6.943	6.839	6.548	6.122
$2\tilde{b}_{12}f_1$	0.0178	0.0169	0.0143	0.0112
$2\tilde{b}_{22}f_2$	−0.620	−0.598	−0.538	−0.457
$3\tilde{c}_{12}f_1$	-1.29×10^{-3}	-1.24×10^{-3}	-1.04×10^{-3}	-7.46×10^{-4}
$3\tilde{c}_{22}f_2$	0.0485	0.0459	0.0391	0.0306
$1+(\tilde{a}_{11}+\tilde{a}_{12})f_1$	6.025	5.731	5.064	4.389
$1+(\tilde{a}_{21}+\tilde{a}_{22})f_2$	6.825	6.261	4.988	3.698
$2(\tilde{b}_{11}+\tilde{b}_{12}+\tilde{b}_{13})f_1$	−0.388	−0.600	−0.921	−0.994
$2(\tilde{b}_{21}+\tilde{b}_{22}+\tilde{b}_{23})f_2$	−0.827	−1.232	−1.845	−1.984
$3(\tilde{c}_{11}+\tilde{c}_{12}+\tilde{c}_{13}+\tilde{c}_{14})f_1$	0.0468	0.114	0.336	0.573
$3(\tilde{c}_{21}+\tilde{c}_{22}+\tilde{c}_{23}+\tilde{c}_{24})f_2$	0.0880	0.216	0.640	1.094

one of the components for the same relative mixture compositions illustrated in these figures. It can be seen that some of the low frequency asymptotic values of the FRFs derivatives increase and some of them decrease for higher amounts of ethyl benzoate present in the mixture. The difference between the given low frequency asymptotic values corresponding to the relative composition of 1:1 and 10:1 is in some cases two orders of magnitude.

The FRFs corresponding to ethyl benzoate and 4-tert-butylphenol are calculated also for different relative compositions of the mixture when the concentration of 4-tert-butylphenol increases (C_{s1}:C_{s2} = 1:1, 1:2, 1:5 and 1:10).

Since the obtained FRFs exhibit shapes very similar to already illustrated ones, the figures corresponding to this studied case are omitted. An observation obtained from comparison of the amplitudes of ($F^*_{1,C2}(\omega)$, $F^*_{2,C2}(\omega,\omega)$ and $F^*_{3,C2}(\omega,\omega,\omega)$) is that the highest ones are for the relative mixture composition of 1:1 and then they decrease for other relative compositions, which is related with an increase of the amount of 4-tert-butylphenol in the mixture. The low frequency asymptotic values of the FRFs derivatives are given in Table 4. It can be noticed that in the case of the inlet concentration change of only one component at the input, either ethyl benzoate or 4-tert-butylphenol, the absolute values of the low frequency asymptotes of the FRFs derivatives decrease with an increase of the amount of 4-tert-butylphenol in the mixture. Again, it can be noticed that some low frequency asymptotic values of the FRF derivatives are at least one order of magnitude lower than the other values in Table 4.

5 Correlation of the FRFs and isotherm parameters

One of the main results obtained from the analysis of the nonlinear FR of a chromatographic column for single adsorbing compound is that the absolute values of the dimensionless coefficients of the single solute adsorption isotherm, which are proportional to local isotherm derivatives, can be estimated from the low frequency asymptotes of the first derivatives of the corresponding FRFs (Ilić et al. 2007b, 2007c; Petkovska and Seidel-Morgenstern 2005). The signs of these coefficients are opposite from the signs of the low frequency asymptotic value of the corresponding FRF phases, which can be $\pm\pi/2$. In this work it is assumed that the coefficients of the dimensionless competitive adsorption isotherm can be also estimated from the low frequency asymptotes of the FRFs phases and their first derivatives.

5.1 Estimation of signs of the dimensionless competitive isotherm coefficients

Comparing the low frequency asymptotic values of the phases of the FRFs illustrated in Figs. 2–10 and values of the corresponding products given in Tables 2–4, it can be noticed that the signs of these products are opposite from the low frequency asymptotic values of the phases. Therefore the signs of the coefficients of the dimensionless competitive isotherm can be estimated from the low frequency asymptotic values of the phases of the corresponding FRFs, which can be $\pm\pi/2$, similar as for the single solute adsorption isotherm (Ilić et al. 2007b, 2007c; Petkovska and Seidel-Morgenstern 2005).

5.2 Estimation of absolute values of the dimensionless competitive isotherm coefficients

In order to find correlations between the absolute values of the coefficients of the dimensionless competitive adsorption isotherm, which are proportional to local partial derivatives of competitive isotherm, and the absolute values of the low frequency asymptotes of the first derivatives of the FRFs, these absolute values are plotted versus the products of the corresponding dimensionless coefficients and factor f_i. The FRFs calculated for different steady-state concentrations of both components in the concentration range from 0.1 g/l up to 35 g/l as well as for different relative compositions of the mixture (1:1, 1:5, 5:1, 1:10 and 10:1) are analyzed.

The absolute values of the low frequency asymptotes of the FRF first derivatives plotted vs. the products of the corresponding dimensionless coefficients and factor f_i when only the concentration of the component 1 changes periodically, while the concentration of the component 2 is constant, at the inlet are given in Figs. 11–12.

It can be seen, that all plots are linear. The same is valid for the single component adsorption (Petkovska and Seidel-Morgenstern 2005). The following equations describe these presented results:

$$\lim_{\omega\to 0}\left|\frac{dG^*_{1,C1}(\omega)}{d\omega}\right| = 1+\tilde{a}_{11}f_1,\qquad \lim_{\omega\to 0}\left|\frac{dF^*_{1,C1}(\omega)}{d\omega}\right| = |\tilde{a}_{21}|f_2, \tag{25a}$$

$$\lim_{\omega\to 0}\left|\frac{dG^*_{2,C1}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{11}|f_1,\qquad \lim_{\omega\to 0}\left|\frac{dF^*_{2,C1}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{21}|f_2, \tag{25b}$$

$$\lim_{\omega\to 0}\left|\frac{dG^*_{3,C1}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{11}|f_1,\qquad \lim_{\omega\to 0}\left|\frac{dF^*_{3,C1}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{21}|f_2. \tag{25c}$$

Similar linear plots are obtained when the concentration of the component 2 changes and the concentration of the component 1 is constant at the inlet, but for the sake of the paper brevity they are not given here. The equations corresponding to them are:

$$\lim_{\omega\to 0}\left|\frac{dG^*_{1,C2}(\omega)}{d\omega}\right| = |\tilde{a}_{12}|f_1,\qquad \lim_{\omega\to 0}\left|\frac{dF^*_{1,C2}(\omega)}{d\omega}\right| = 1+\tilde{a}_{22}f_2, \tag{26a}$$

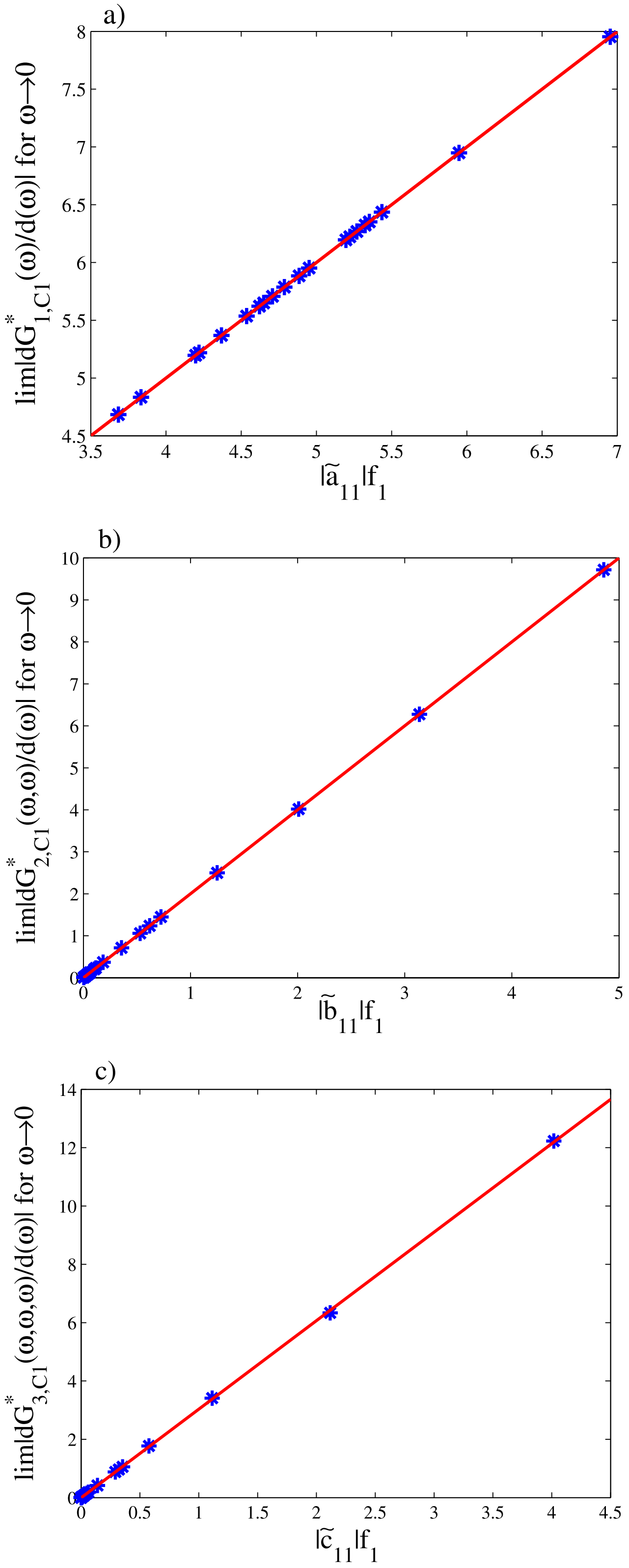


Fig. 11 The amplitude of the low frequency asymptote of the first derivative of: (**a**) $G^*_{1,C1}(\omega)$ vs. $|\tilde{a}_{11}|f_1$, (**b**) $G^*_{2,C1}(\omega,\omega)$ vs. $|\tilde{b}_{11}|f_1$ and (**c**) $G^*_{3,C1}(\omega,\omega,\omega)$ vs. $|\tilde{c}_{11}|f_1$

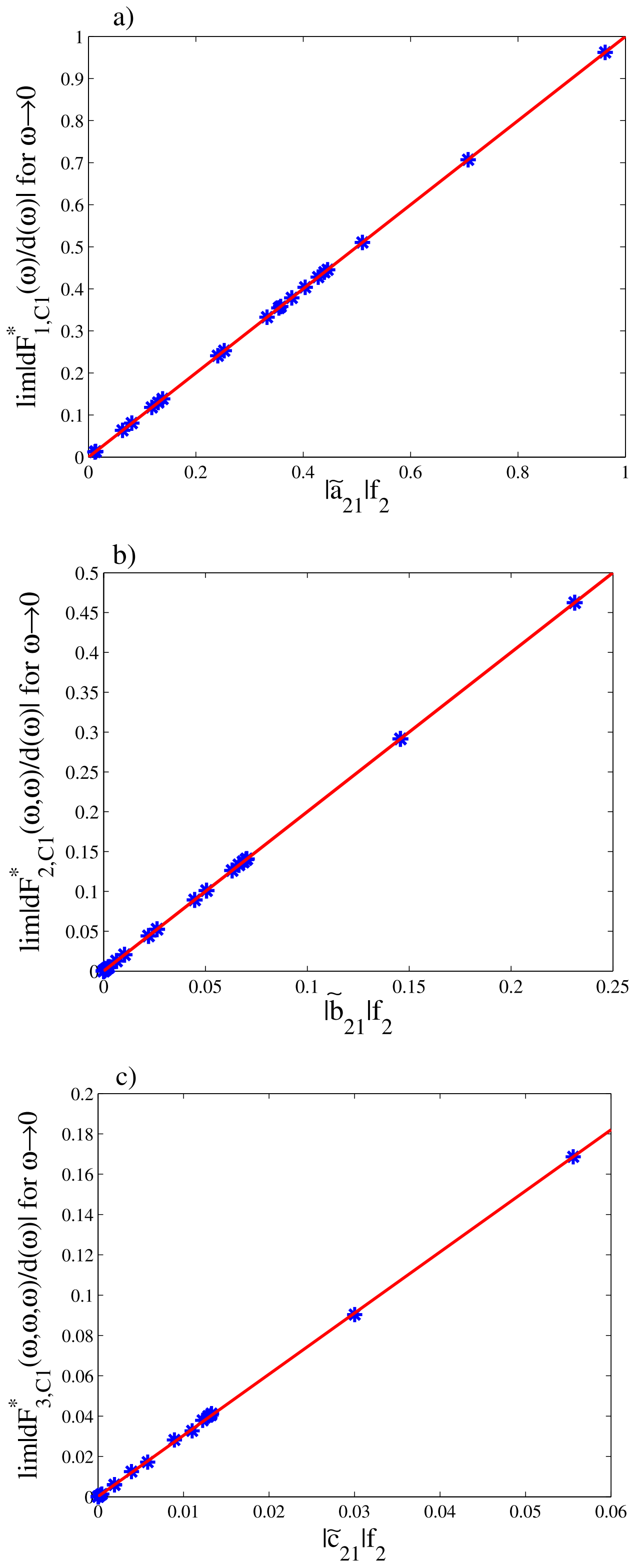


Fig. 12 The amplitude of the low frequency asymptote of the first derivative of: (**a**) $F^*_{1,C1}(\omega)$ vs. $|\tilde{a}_{21}|f_2$, (**b**) $F^*_{2,C1}(\omega,\omega)$ vs. $|\tilde{b}_{21}|f_2$ and (**c**) $F^*_{3,C1}(\omega,\omega,\omega)$ vs. $|\tilde{c}_{21}|f_2$

$$\begin{gathered}\lim_{\omega\to 0}\left|\frac{dG^*_{2,C2}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{12}|f_1,\\ \lim_{\omega\to 0}\left|\frac{dF^*_{2,C2}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{22}|f_2,\end{gathered}\tag{26b}$$

$$\begin{gathered}\lim_{\omega\to 0}\left|\frac{dG^*_{3,C2}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{12}|f_1,\\ \lim_{\omega\to 0}\left|\frac{dF^*_{3,C2}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{22}|f_2.\end{gathered}\tag{26c}$$

As it can be noticed from the above given equations, in order to obtain the coefficients of the competitive adsorption isotherm in the dimensionless form that correspond to terms containing only concentration of the component 1 (c_1, c_1^2, c_1^3), the inlet concentration of this component should be changed periodically while the inlet concentration of the other component is constant. From the calculated FRFs and using (25a–25c), these coefficients are obtained. In a similar way, by changing periodically the inlet concentration of the component 2 and keeping the inlet concentration of the component 1 constant, the coefficients corresponding to terms that contain only concentration of the component 2 (c_2, c_2^2, c_2^3) are calculated from (26a–26c).

For a very accurate estimation of the competitive adsorption isotherm, it is required to calculate also the coefficients that correspond to the cross terms (c_1c_2, $c_1^2c_2$, $c_1c_2^2$), i.e. coefficients which are proportional to mixed partial derivatives. This can be achieved by periodical change of the inlet concentration of both components. The absolute values of the low frequency asymptotes of the first derivatives of the $G_{C1\&C2}$- and $F_{C1\&C2}$-functions are again linearly dependent on the corresponding sum of the coefficients multiplied by f_i. For the same reason as in the previous case, these figures are omitted. The obtained results corresponding to the $G_{C1\&C2}$- and $F_{C1\&C2}$-functions are described by the following equations:

$$\begin{gathered}\lim_{\omega\to 0}\left|\frac{dG^*_{1,C1\&C2}(\omega)}{d\omega}\right| = 1+|\tilde{a}_{11}+\tilde{a}_{12}|f_1,\\ \lim_{\omega\to 0}\left|\frac{dF^*_{1,C1\&C2}(\omega)}{d\omega}\right| = 1+|\tilde{a}_{21}+\tilde{a}_{22}|f_2,\end{gathered}\tag{27a}$$

$$\begin{gathered}\lim_{\omega\to 0}\left|\frac{dG^*_{2,C1\&C2}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{11}+\tilde{b}_{12}+\tilde{b}_{13}|f_1,\\ \lim_{\omega\to 0}\left|\frac{dF^*_{2,C1\&C2}(\omega,\omega)}{d\omega}\right| = 2|\tilde{b}_{21}+\tilde{b}_{22}+\tilde{b}_{23}|f_2,\end{gathered}\tag{27b}$$

$$\lim_{\omega\to 0}\left|\frac{dG^*_{3,C1\&C2}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{11}+\tilde{c}_{12}+\tilde{c}_{13}+\tilde{c}_{14}|f_1,\tag{27c}$$

$$\lim_{\omega\to 0}\left|\frac{dF^*_{3,C1\&C2}(\omega,\omega,\omega)}{d\omega}\right| = 3|\tilde{c}_{21}+\tilde{c}_{22}+\tilde{c}_{23}+\tilde{c}_{24}|f_2.\tag{27d}$$

The coefficients that correspond to the cross terms can be calculated from (27b–27d) if the other coefficients in these equations are already determined. Equation (27b) gives the coefficients $\tilde{b}_{13}$ and $\tilde{b}_{23}$ which correspond to the c_1c_2 term, while (27c) and (27d) give the sum of the coefficients corresponding to the $c_1^2c_2$ and $c_1c_2^2$ terms. A fact that only the sum of the coefficients $\tilde{c}_{13}$ and $\tilde{c}_{14}$, as well as of the coefficients $\tilde{c}_{23}$ and $\tilde{c}_{24}$, can be calculated, but not each of them separately might affect accuracy of the competitive adsorption isotherm estimated by the suggested nonlinear FR method. However, this method gives more information about competitive isotherms in comparison to classical methods, since one can estimate the first three partial derivatives of an isotherm using the nonlinear FR method. The results obtained in this section made the use of the products of the dimensionless coefficients, i.e. their sum, and factor f_i in the first column of Tables 2–4 reasonable.

6 Conclusions

The FRFs of the first, second and third order are derived for the adsorption of two dissolved compounds in a chromatographic column. Two types of the FRFs are considered. One of them (G-functions) relate the concentration changes of the component 1 with the inlet concentration change and the other (F-functions) relate the concentration changes of the component 2 with the inlet concentration change. At the inlet of a chromatographic column the concentration of one of two components or both can be varied periodically. The FRFs corresponding to different steady-state concentrations (here 1, 5, 10 and 15 g/l) and relative compositions of a model mixture (here ethyl benzoate and 4-tert-butylphenol, C_{s1}:C_{s2} = 1:1, 1:2, 2:1, 1:5, 5:1, 1:10 and 10:1) are analyzed. Although the calculated FRFs differ, certain similarity in their shapes can be noticed. Depending on the inlet concentration change the amplitude of the first order FRFs of both components tend to 1 or 0 for low frequencies and to 0 for high frequencies. In some cases, the amplitude has maximum in the frequency range from 0.01 to 0.1 rad/s above 1. The phase of the first order FRFs has an asymptote in the low frequency range (0 or $+\pi/2$) and it tends to $-\infty$ for higher frequencies. The amplitudes of the second and third order FRFs corresponding to both components have similar shapes regardless of the inlet concentration change. They tend to 0 for both low and high frequencies and have a maximum in the same frequency range as the first order FRFs. Similar to the phases of the first order FRFs, the phases of the second and third order FRFs have an asymptote in the low frequency range ($\pm\pi/2$) and tend to $-\infty$ at higher frequencies. The low frequency asymptotic values of the first derivatives of the FRFs changes (increases or decreases) with an increase of the steady-state concentration and the amount of ethyl benzoate or 4-tert-butylphenol present in the mixture. Differences in the asymptotic values of the FRFs corresponding to some of the analyzed cases are even two orders of magnitude.

As the most important result of the presented analysis, it has been found that the FRFs can be used for estimation of local partial derivatives of competitive adsorption isotherms at different concentrations. The signs of the corresponding isotherm derivatives can be obtained from the low frequency asymptotes of the phases of the FRFs and the absolute values of these isotherm derivatives can be estimated from the low frequency asymptotic values of the first derivatives of the corresponding FRFs (25a–27d). There are certain limits in estimation of all dimensionless isotherm coefficients, because only the sum of the coefficients corresponding to some cross terms can be estimated. Nevertheless, a lot of information about the equilibrium behavior of the system under investigation is gathered from other experimentally obtained coefficients, which are proportional to partial isotherm derivatives. Furthermore, inflection points can be detected easily based on the sign change of the second order FRF when concentration of both components is changed at the inlet of a column.

Acknowledgements The authors are grateful to Daliborka Nikolić (Belgrade University) for initial work related to the problem investigated. This work was partly supported by the Serbian Ministry of Science and Environmental Protection in the frame of Project No. 142014 and Fonds der Chemischen Industrie.

Appendix

Dimensionless concentration in the solid phase at the distance x from the column inlet expressed in the Volterra series form is:

$$
\begin{aligned}
q_i(x,t) = \tilde{a}_{i1}\Bigg(&\frac{A}{2}G_1(x,\omega)e^{j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^2 G_2(x,\omega,\omega)e^{2j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^3 G_3(x,\omega,\omega,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{a}_{i2}\Bigg(\frac{A}{2}F_1(x,\omega)e^{j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^2 F_2(x,\omega,\omega)e^{2j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^3 F_3(x,\omega,\omega,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{b}_{i1}\Bigg(\left(\frac{A}{2}\right)^2 G_1^2(x,\omega)e^{2j\omega t} + \cdots \\
&+ 2\left(\frac{A}{2}\right)^3 G_1(x,\omega)G_2(x,\omega,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{b}_{i2}\Bigg(\left(\frac{A}{2}\right)^2 F_1^2(x,\omega)e^{2j\omega t} + \cdots \\
&+ 2\left(\frac{A}{2}\right)^3 F_1(x,\omega)F_2(x,\omega,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{b}_{i3}\Bigg(\left(\frac{A}{2}\right)^2 G_1(x,\omega)F_1(x,\omega)e^{2j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^3 G_1(x,\omega)F_2(x,\omega,\omega)e^{3j\omega t} + \cdots \\
&+ \left(\frac{A}{2}\right)^3 G_2(x,\omega,\omega)F_1(x,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{c}_{i1}\Bigg(\left(\frac{A}{2}\right)^3 G_1^3(x,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{c}_{i2}\Bigg(\left(\frac{A}{2}\right)^3 F_1^3(x,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{c}_{i3}\Bigg(\left(\frac{A}{2}\right)^3 G_1^2(x,\omega)F_1(x,\omega)e^{3j\omega t} + \cdots\Bigg) \\
&+ \tilde{c}_{i4}\Bigg(\left(\frac{A}{2}\right)^3 G_1(x,\omega)F_1^2(x,\omega)e^{3j\omega t} + \cdots\Bigg), \\
i = 1,2. &\qquad (28)
\end{aligned}
$$

A detailed procedure for derivation of the FRFs which relate the concentration of the component 1 (G-functions) and component 2 (F-functions) in the liquid phase at distance x from the column inlet to the inlet concentration change will be given below. Equations corresponding to the FRFs that relate the outlet concentration to the inlet concentration change are also provided. These functions are denoted by an asterisk in the superscript ($G*$, $F*$).

First order FRFs $G_1(x,\omega)$ and $F_1(x,\omega)$

In this section the first order FRFs at the distance x from the column inlet of both components ($G_1(x,\omega)$ and $F_1(x,\omega)$), as well as at the column outlet ($G_1(x=1,\omega) = G_1^*(\omega)$ and $F_1(x=1,\omega) = F_1^*(\omega)$), will be derived. The first order FRF is proportional to the dominant term of the first harmonic in the output and only terms containing $(A/2)e^{j\omega t}$ are of interest (Weiner and Spina 1980). By introducing (23) and (28) for the component 1 into the model equation (11), then collecting terms which contain $(A/2)e^{j\omega t}$ and equating them to zero the following equation is obtained:

$$
\begin{aligned}
&\frac{d^2G_1(x,\omega)}{dx^2} - 2N_{tp}\frac{dG_1(x,\omega)}{dx} \\
&\quad - 2N_{tp}j\omega(1 + f_1\tilde{a}_{11})G_1(x,\omega) \\
&\quad - 2N_{tp}j\omega f_1\tilde{a}_{12}F_1(x,\omega) = 0. \qquad (29a)
\end{aligned}
$$

Similarly, introducing (23) and (28) for the component 2 into (11) yields:

$$\begin{aligned}&\frac{d^2F_1(x,\omega)}{dx^2}-2N_{tp}\frac{dF_1(x,\omega)}{dx}\\&\quad-2N_{tp}j\omega(1+f_2\tilde{a}_{22})F_1(x,\omega)\\&\quad-2N_{tp}j\omega f_2\tilde{a}_{21}G_1(x,\omega)=0.\end{aligned}\tag{29b}$$

In order to obtain the boundary conditions in the Volterra series form in the case when the concentration of only one component (e.g. component 1) is varied at the inlet (21) and (23) are introduced into the boundary conditions denoted by (17). Collecting terms which contain $(A/2)e^{j\omega t}$ and equating them to zero yields:

$$\begin{aligned}x=0:\quad &G_1(0,\omega)=1+\frac{1}{2N_{tp}}\cdot\left.\frac{dG_1(x,\omega)}{dx}\right|_{x=0};\\&F_1(0,\omega)=\frac{1}{2N_{tp}}\cdot\left.\frac{dF_1(x,\omega)}{dx}\right|_{x=0},\end{aligned}\tag{30a}$$

$$x=1:\quad \left.\frac{dG_1(x,\omega)}{dx}\right|_{x=1}=0;\qquad \left.\frac{dF_1(x,\omega)}{dx}\right|_{x=1}=0.\tag{30b}$$

If the concentration of both components is varied at the inlet, the boundary conditions are obtained in a similar way introducing (22) instead of (21) into (17). Then the following equations for the boundary conditions in the Volterra series are obtained:

$$\begin{aligned}x=0:\quad &G_1(0,\omega)=1+\frac{1}{2N_{tp}}\cdot\left.\frac{dG_1(x,\omega)}{dx}\right|_{x=0};\\&F_1(0,\omega)=1+\frac{1}{2N_{tp}}\cdot\left.\frac{dF_1(x,\omega)}{dx}\right|_{x=0},\end{aligned}\tag{31a}$$

$$x=1:\quad \frac{dG_1(x,\omega)}{dx}|_{x=1}=0;\qquad \left.\frac{dF_1(x,\omega)}{dx}\right|_{x=1}=0.\tag{31b}$$

Combination of (29a) and (29b) gives:

$$\begin{aligned}&\frac{d^4G_1(x,\omega)}{dx^4}-4N_{tp}\frac{d^3G_1(x,\omega)}{dx^3}+r_{G_1,1}\frac{d^2G_1(x,\omega)}{dx^2}\\&\quad+r_{G_1,2}\frac{dG_1(x,\omega)}{dx}+r_{G_1,3}G_1(x,\omega)=0,\end{aligned}\tag{32a}$$

$$\begin{aligned}&\frac{d^4F_1(x,\omega)}{dx^4}-4N_{tp}\frac{d^3F_1(x,\omega)}{dx^3}+r_{F_1,1}\frac{d^2F_1(x,\omega)}{dx^2}\\&\quad+r_{F_1,2}\frac{dF_1(x,\omega)}{dx}+r_{F_1,3}F_1(x,\omega)=0\end{aligned}\tag{32b}$$

where coefficients $r_{G_1,i}$ and $r_{F_1,i}$ are defined as follows:

$$\begin{aligned}r_{G_1,1}&=r_{F_1,1}=r_{G_1/F_1,1}\\&=4N_{tp}^2-2N_{tp}j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}),\end{aligned}\tag{33a}$$

$$\begin{aligned}r_{G_1,2}&=r_{F_1,2}=r_{G_1/F_1,2}\\&=4N_{tp}^2j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}),\end{aligned}\tag{33b}$$

$$\begin{aligned}r_{G_1,3}&=r_{F_1,3}=r_{G_1/F_1,3}\\&=4N_{tp}^2\omega^2(f_1f_2(\tilde{a}_{12}\tilde{a}_{21}-\tilde{a}_{11}\tilde{a}_{22})\\&\qquad-f_1\tilde{a}_{11}-f_2\tilde{a}_{22}-1).\end{aligned}\tag{33c}$$

Equations (32a) and (32b) are linear, homogeneous ordinary differential equations (ODEs) of the fourth order with constant coefficients. Their solution has the following general form:

$$\begin{aligned}G_1(x,\omega)&=P_{G_1,1}e^{\chi_{G_1,1}x}+P_{G_1,2}e^{\chi_{G_1,2}x},\\&\quad+P_{G_1,3}e^{\chi_{G_1,3}x}+P_{G_1,4}e^{\chi_{G_1,4}x},\end{aligned}\tag{34a}$$

$$\begin{aligned}F_1(x,\omega)&=P_{F_1,1}e^{\chi_{F_1,1}x}+P_{F_1,2}e^{\chi_{F_1,2}x}\\&\quad+P_{F_1,3}e^{\chi_{F_1,3}x}+P_{F_1,4}e^{\chi_{F_1,4}x}\end{aligned}\tag{34b}$$

where $\chi_{G_1,i}$ and $\chi_{F_1,i}$ are the solutions of the corresponding characteristic equation, given by (35):

$$\begin{aligned}&\chi_{G_1/F_1}^4-4N_{tp}\chi_{G_1/F_1}^3+r_{G_1/F_1,1}\chi_{G_1/F_1}^2\\&\quad+r_{G_1/F_1,2}\chi_{G_1/F_1}+r_{G_1/F_1,3}=0.\end{aligned}\tag{35}$$

Since the coefficients $r_{G_1,i}$ and $r_{F_1,i}$ are equal (33a–33c), then is also valid $\chi_{G_1,i}=\chi_{F_1,i}=\chi_{G_1/F_1,i}$. A correlation between the integration constants $P_{G_1,1}$ to $P_{G_1,4}$ and $P_{F_1,1}$ to $P_{F_1,4}$ can be obtained by introducing (34a) and (34b) into (29a) and (29b), whereby the $P_{F_1,i}$ constant can be expressed as a function of the $P_{G_1,i}$ constant:

$$\begin{aligned}&P_{F_1,i}=P_{G_1,i}\frac{\chi_{G_1,i}^2-2N_{tp}\chi_{G_1,i}-2N_{tp}j\omega(1+f_1\tilde{a}_{11})}{2N_{tp}j\omega f_1\tilde{a}_{12}},\\&\quad i=1,2,3,4.\end{aligned}\tag{36}$$

By introducing (34a), (34b) and (36) into (30a–30b) or (31a–31b) (depending on the case that should be solved) a system of four equations with four unknown variables is obtained. As a result of solving this system the integration constants $P_{G_1,i}$ are calculated. The analytical expressions are very complex and therefore will not be given in this paper.

The final forms of the first order FRFs for both components on the column scale can be written in the following general form:

$$\begin{aligned}G_1^*(\omega)&=G_1(1,\omega)\\&=P_{G_1,1}e^{\chi_{G_1,1}}+P_{G_1,2}e^{\chi_{G_1,2}}\\&\quad+P_{G_1,3}e^{\chi_{G_1,3}}+P_{G_1,4}e^{\chi_{G_1,4}},\end{aligned}\tag{37a}$$

$$\begin{aligned}F_1^*(\omega)&=F_1(1,\omega)\\&=P_{F_1,1}e^{\chi_{F_1,1}}+P_{F_1,2}e^{\chi_{F_1,2}}\\&\quad+P_{F_1,3}e^{\chi_{F_1,3}}+P_{F_1,4}e^{\chi_{F_1,4}}.\end{aligned}\tag{37b}$$

Second order FRFs $G_2(x,\omega,\omega)$ and $F_2(x,\omega,\omega)$

A procedure for derivation of the second order FRFs at the distance x from the column inlet of both components ($G_2(x,\omega,\omega)$ and $F_2(x,\omega,\omega)$) and at the column outlet ($G_2(x=1,\omega,\omega)=G_2^*(\omega,\omega)$ and $F_2(x=1,\omega,\omega)=F_2^*(\omega,\omega)$) is the same as for the first order FRF, except that terms containing $(A/2)^2e^{2j\omega t}$ instead of $(A/2)e^{j\omega t}$ are collected. These second order FRFs correspond to the dominant term of the second harmonic in the output (Weiner and Spina 1980). The following equations define the second order FRFs $G_2(x,\omega,\omega)$ and $F_2(x,\omega,\omega)$:

$$\begin{aligned}&\frac{d^2G_2(x,\omega,\omega)}{dx^2}-2N_{tp}\frac{dG_2(x,\omega,\omega)}{dx}\\&\quad-4N_{tp}j\omega(1+f_1\tilde{a}_{11})G_2(x,\omega,\omega)\\&\quad-4N_{tp}j\omega f_1\tilde{a}_{12}F_2(x,\omega,\omega)=R_{G_2}(x,\omega,\omega),\end{aligned}\tag{38a}$$

$$\begin{aligned}&\frac{d^2F_2(x,\omega,\omega)}{dx^2}-2N_{tp}\frac{dF_2(x,\omega,\omega)}{dx}\\&\quad-4N_{tp}j\omega(1+f_2\tilde{a}_{22})F_2(x,\omega,\omega)\\&\quad-4N_{tp}j\omega f_2\tilde{a}_{21}G_2(x,\omega,\omega)=R_{F_2}(x,\omega,\omega)\end{aligned}\tag{38b}$$

where $R_{G_2}(x,\omega,\omega)$ is:

$$\begin{aligned}R_{G_2}(x,\omega,\omega)&=4N_{tp}j\omega f_1(\tilde{b}_{11}G_1^2(x,\omega)+\tilde{b}_{12}F_1^2(x,\omega)\\&\quad+\tilde{b}_{13}G_1(x,\omega)F_1(x,\omega))\end{aligned}\tag{39a}$$

and $R_{F_2}(x,\omega,\omega)$:

$$\begin{aligned}R_{F_2}(x,\omega,\omega)&=4N_{tp}j\omega f_2(\tilde{b}_{21}G_1^2(x,\omega)+\tilde{b}_{22}F_1^2(x,\omega)\\&\quad+\tilde{b}_{23}G_1(x,\omega)F_1(x,\omega)).\end{aligned}\tag{39b}$$

The boundary conditions in the Volterra series form are the same regardless whether the concentration of only one or both components is varied at the inlet and can be written as:

$$\begin{aligned}x=0:\quad &G_2(0,\omega,\omega)=\frac{1}{2N_{tp}}\cdot\left.\frac{dG_2(x,\omega,\omega)}{dx}\right|_{x=0};\\&F_2(0,\omega,\omega)=\frac{1}{2N_{tp}}\cdot\left.\frac{dF_2(x,\omega,\omega)}{dx}\right|_{x=0},\end{aligned}\tag{40a}$$

$$\begin{aligned}x=1:\quad &\left.\frac{dG_2(x,\omega,\omega)}{dx}\right|_{x=1}=0;\\&\left.\frac{dF_2(x,\omega,\omega)}{dx}\right|_{x=1}=0.\end{aligned}\tag{40b}$$

The following equations are obtained from combination of (38a) and (38b):

$$\begin{aligned}&\frac{d^4G_2(x,\omega,\omega)}{dx^4}-4N_{tp}\frac{d^3G_2(x,\omega,\omega)}{dx^3}\\&\quad+r_{G_2,1}\frac{d^2G_2(x,\omega,\omega)}{dx^2}+r_{G_2,2}\frac{dG_2(x,\omega,\omega)}{dx}\\&\quad+r_{G_2,3}G_2(x,\omega,\omega)\\&=4N_{tp}j\omega f_1\tilde{a}_{12}R_{F_2}(x,\omega,\omega)+\frac{d^2R_{G_2}(x,\omega,\omega)}{dx^2}\\&\quad-2N_{tp}\frac{dR_{G_2}(x,\omega,\omega)}{dx}\\&\quad-4N_{tp}j\omega(1+f_2\tilde{a}_{22})R_{G_2}(x,\omega,\omega),\end{aligned}\tag{41a}$$

$$\begin{aligned}&\frac{d^4F_2(x,\omega,\omega)}{dx^4}-4N_{tp}\frac{d^3F_2(x,\omega,\omega)}{dx^3}\\&\quad+r_{F_2,1}\frac{d^2F_2(x,\omega,\omega)}{dx^2}+r_{F_2,2}\frac{dF_2(x,\omega,\omega)}{dx}\\&\quad+r_{F_2,3}F_2(x,\omega,\omega)\\&=4N_{tp}j\omega f_2\tilde{a}_{21}R_{G_2}(x,\omega,\omega)+\frac{d^2R_{F_2}(x,\omega,\omega)}{dx^2}\\&\quad-2N_{tp}\frac{dR_{F_2}(x,\omega,\omega)}{dx}\\&\quad-4N_{tp}j\omega(1+f_1\tilde{a}_{11})R_{F_2}(x,\omega,\omega)\end{aligned}\tag{41b}$$

where coefficients $r_{G_2,i}$ and $r_{F_2,i}$ are:

$$\begin{aligned}r_{G_2,1}&=r_{F_2,1}=r_{G_2/F_2,1}\\&=4N_{tp}^2-4N_{tp}j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}),\end{aligned}\tag{42a}$$

$$\begin{aligned}r_{G_2,2}&=r_{F_2,2}=r_{G_2/F_2,2}\\&=8N_{tp}^2j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}),\end{aligned}\tag{42b}$$

$$\begin{aligned}r_{G_2,3}&=r_{F_2,3}=r_{G_2/F_2,3}\\&=16N_{tp}^2\omega^2(f_1f_2(\tilde{a}_{12}\tilde{a}_{21}-\tilde{a}_{11}\tilde{a}_{22})\\&\quad-f_1\tilde{a}_{11}-f_2\tilde{a}_{22}-1).\end{aligned}\tag{42c}$$

Equations (41a) and (41b) are linear, nonhomogeneous fourth-order ODEs with constant coefficients. Their solution is of the following general form:

$$\begin{aligned}&G_2(x,\omega,\omega)\\&=P_{G_2,1}e^{\chi_{G_2,1}x}+P_{G_2,2}e^{\chi_{G_2,2}x}+P_{G_2,3}e^{\chi_{G_2,3}x}\\&\quad+P_{G_2,4}e^{\chi_{G_2,4}x}+p_{G_2,1}e^{2\chi_{G_1,1}x}+p_{G_2,2}e^{2\chi_{G_1,2}x}\\&\quad+p_{G_2,3}e^{2\chi_{G_1,3}x}+p_{G_2,4}e^{2\chi_{G_1,4}x}\\&\quad+p_{G_2,5}e^{(\chi_{G_1,1}+\chi_{G_1,2})x}+p_{G_2,6}e^{(\chi_{G_1,1}+\chi_{G_1,3})x}\\&\quad+p_{G_2,7}e^{(\chi_{G_1,1}+\chi_{G_1,4})x}+p_{G_2,8}e^{(\chi_{G_1,2}+\chi_{G_1,3})x}\\&\quad+p_{G_2,9}e^{(\chi_{G_1,2}+\chi_{G_1,4})x}+p_{G_2,10}e^{(\chi_{G_1,3}+\chi_{G_1,4})x},\end{aligned}\tag{43a}$$

$$
\begin{aligned}
&F_2(x,\omega,\omega)\\
&\quad= P_{F_2,1}e^{\chi_{F_2,1}x}+P_{F_2,2}e^{\chi_{F_2,2}x}+P_{F_2,3}e^{\chi_{F_2,3}x}\\
&\qquad+P_{F_2,4}e^{\chi_{F_2,4}x}+p_{F_2,1}e^{2\chi_{F_1,1}x}+p_{F_2,2}e^{2\chi_{F_1,2}x}\\
&\qquad+p_{F_2,3}e^{2\chi_{F_1,3}x}+p_{F_2,4}e^{2\chi_{F_1,4}x}\\
&\qquad+p_{F_2,5}e^{(\chi_{F_1,1}+\chi_{F_1,2})x}+p_{F_2,6}e^{(\chi_{F_1,1}+\chi_{F_1,3})x}\\
&\qquad+p_{F_2,7}e^{(\chi_{F_1,1}+\chi_{F_1,4})x}+p_{F_2,8}e^{(\chi_{F_1,2}+\chi_{F_1,3})x}\\
&\qquad+p_{F_2,9}e^{(\chi_{F_1,2}+\chi_{F_1,4})x}+p_{F_2,10}e^{(\chi_{F_1,3}+\chi_{F_1,4})x}
\end{aligned}
\tag{43b}
$$

where $\chi_{G_2,i}$ and $\chi_{F_2,i}$ are solutions of the corresponding characteristic equation, given as:

$$
\begin{aligned}
&\chi^4_{G_2/F_2}-4N_{tp}\chi^3_{G_2/F_2}+r_{G_2/F_2,1}\chi^2_{G_2/F_2}+r_{G_2/F_2,2}\chi_{G_2/F_2}\\
&\quad+r_{G_2/F_2,3}=0.
\end{aligned}
\tag{44}
$$

Since the coefficients $r_{G_2,i}$ and $r_{F_2,i}$ are equal, (42a–42c), then the coefficients $\chi_{G_2,i}$, $\chi_{F_2,i}$ and $\chi_{G_2/F_2,i}$ are also equal. The integration constants $p_{G_2,1}$ to $p_{G_2,10}$ and $p_{F_2,1}$ to $p_{F_2,10}$ are calculated by introducing the particular solutions of the corresponding second order FRFs into (41a) and (41b).

Integration constants in (43a) are:

$$
\begin{aligned}
p^{num}_{G_2,i}&=4N_{tp}j\omega f_1\{4N_{tp}j\omega f_2\tilde{a}_{12}\\
&\qquad\times(\tilde{b}_{21}P^2_{G_1,i}+\tilde{b}_{22}P^2_{F_1,i}+\tilde{b}_{23}P_{G_1,i}P_{F_1,i})\\
&\qquad+(4\chi^2_{G_1,i}-4N_{tp}\chi_{G_1,i}-4N_{tp}j\omega(1+f_2\tilde{a}_{22}))\\
&\qquad\times(\tilde{b}_{11}P^2_{G_1,i}+\tilde{b}_{12}P^2_{F_1,i}+\tilde{b}_{13}P_{G_1,i}P_{F_1,i})\},
\end{aligned}
\tag{45}
$$

$$
\begin{aligned}
p^{den}_{G_2,i}&=16\chi^4_{G_1,i}-32N_{tp}\chi^3_{G_1,i}+4r_{G_2,1}\chi^2_{G_1,i}\\
&\qquad+2r_{G_2,2}\chi_{G_1,i}+r_{G_2,3},\\
p_{G_2,i}&=\frac{p^{num}_{G_2,i}}{p^{den}_{G_2,i}},\qquad i=1,2,3,4
\end{aligned}
$$

$$
\begin{aligned}
p^{num}_{G_2,k}&=4N_{tp}j\omega f_1\{4N_{tp}j\omega f_2\tilde{a}_{12}(2\tilde{b}_{21}P_{G_1,i}P_{G_1,j}\\
&\qquad+2\tilde{b}_{22}P_{F_1,i}P_{F_1,j}\\
&\qquad+\tilde{b}_{23}(P_{G_1,i}P_{F_1,j}+P_{G_1,j}P_{F_1,i}))\\
&\qquad+((\chi_{G_1,i}+\chi_{G_1,j})^2-2N_{tp}(\chi_{G_1,i}+\chi_{G_1,j})\\
&\qquad-4N_{tp}j\omega(1+f_2\tilde{a}_{22}))(2\tilde{b}_{11}P_{G_1,i}P_{G_1,j}\\
&\qquad+2\tilde{b}_{12}P_{F_1,i}P_{F_1,j}\\
&\qquad+\tilde{b}_{13}(P_{G_1,i}P_{F_1,j}+P_{G_1,j}P_{F_1,i}))\},
\end{aligned}
\tag{46}
$$

$$
\begin{aligned}
p^{den}_{G_2,k}&=(\chi_{G_1,i}+\chi_{G_1,j})^4-4N_{tp}(\chi_{G_1,i}+\chi_{G_1,j})^3\\
&\qquad+r_{G_2,1}(\chi_{G_1,i}+\chi_{G_1,j})^2\\
&\qquad+r_{G_2,2}(\chi_{G_1,i}+\chi_{G_1,j})+r_{G_2,3},
\end{aligned}
$$

Table 5 Combination of indexes for $p_{G_2,5}$–$p_{G_2,10}$ and $p_{F_2,5}$–$p_{F_2,10}$

k	i	j	**k**	i	j
5	1	2	**8**	2	3
6	1	3	**9**	2	4
7	1	4	**10**	3	4

$$
\begin{aligned}
p_{G_2,k}&=\frac{p^{num}_{G_2,k}}{p^{den}_{G_2,k}},\qquad k=5,6,\ldots,10;\\
&i=1,2,3;\ \ j=2,3,4;\ \ i\neq j
\end{aligned}
$$

and combination of subscripts is given in Table 5.

Integration constants in (43b) are:

$$
\begin{aligned}
p^{num}_{F_2,i}&=p_{G_2,i}(4\chi^2_{F_1,i}-4N_{tp}\chi_{F_1,i}-4N_{tp}j\omega(1+f_1\tilde{a}_{11}))\\
&\qquad-4N_{tp}j\omega f_1(\tilde{b}_{11}P^2_{G_1,i}+\tilde{b}_{12}P^2_{F_1,i}\\
&\qquad+\tilde{b}_{13}P_{G_1,i}P_{F_1,i}),\\
p_{F_2,i}&=\frac{p^{num}_{F_2,i}}{4N_{tp}j\omega f_1\tilde{a}_{12}},\qquad i=1,2,3,4,
\end{aligned}
\tag{47}
$$

$$
\begin{aligned}
p^{num}_{F_2,k}&=p_{G_2,k}((\chi_{F_1,i}+\chi_{F_1,j})^2-2N_{tp}(\chi_{F_1,i}+\chi_{F_1,j})\\
&\qquad-4N_{tp}j\omega(1+f_1\tilde{a}_{11}))-4N_{tp}j\omega f_1\\
&\qquad\times(2\tilde{b}_{11}P_{G_1,i}P_{G_1,j}+2\tilde{b}_{12}P_{F_1,i}P_{F_1,j}\\
&\qquad+\tilde{b}_{13}(P_{G_1,i}P_{F_1,j}+P_{G_1,j}P_{F_1,i})),\\
p_{F_2,k}&=\frac{p^{num}_{F_2,k}}{4N_{tp}j\omega f_1\tilde{a}_{12}},\qquad k=5,6,\ldots,10;\ i=1,2,3;\\
&j=2,3,4;\ \ i\neq j
\end{aligned}
\tag{48}
$$

where combination of subscripts is same as for the p_{G_2}-constants and is given in Table 5.

Correlations between the integration constants $P_{G_2,1}$ to $P_{G_2,4}$ and $P_{F_2,1}$ to $P_{F_2,4}$ are obtained from (38a), (38b), (43a) and (43b), whereby the $P_{F_2,i}$ constant can be expressed as a function of the $P_{G_2,i}$ constant as follows:

$$
\begin{aligned}
P_{F_2,i}&=P_{G_2,i}\frac{\chi^2_{G_2,i}-2N_{tp}\chi_{G_2,i}-4N_{tp}j\omega(1+f_1\tilde{a}_{11})}{4N_{tp}j\omega f_1\tilde{a}_{12}},\\
&i=1,2,3,4.
\end{aligned}
\tag{49}
$$

By introducing (43a), (43b) and (49) into (40a) and (40b), a system of four equations with four unknown variables is obtained. The integration constants $P_{G_2,i}$ are calculated as a result of solving this system of equations. Due to complexity of their analytical expressions, they will not be given in this paper.

The second order FRFs for both components on the column scale can be expressed in the following general form:

$$\begin{aligned}
G_2^*(\omega,\omega) &= G_2(1,\omega,\omega)\\
&= P_{G_2,1}e^{\chi_{G_2,1}} + P_{G_2,2}e^{\chi_{G_2,2}}\\
&\quad + P_{G_2,3}e^{\chi_{G_2,3}} + P_{G_2,4}e^{\chi_{G_2,4}} + p_{G_2,1}e^{2\chi_{G_1,1}}\\
&\quad + p_{G_2,2}e^{2\chi_{G_1,2}} + p_{G_2,3}e^{2\chi_{G_1,3}} + p_{G_2,4}e^{2\chi_{G_1,4}}\\
&\quad + p_{G_2,5}e^{\chi_{G_1,1}+\chi_{G_1,2}} + p_{G_2,6}e^{\chi_{G_1,1}+\chi_{G_1,3}}\\
&\quad + p_{G_2,7}e^{\chi_{G_1,1}+\chi_{G_1,4}} + p_{G_2,8}e^{\chi_{G_1,2}+\chi_{G_1,3}}\\
&\quad + p_{G_2,9}e^{\chi_{G_1,2}+\chi_{G_1,4}}\\
&\quad + p_{G_2,10}e^{\chi_{G_1,3}+\chi_{G_1,4}}, \qquad (50a)
\end{aligned}$$

$$\begin{aligned}
F_2^*(\omega,\omega) &= F_2(1,\omega,\omega)\\
&= P_{F_2,1}e^{\chi_{F_2,1}} + P_{F_2,2}e^{\chi_{F_2,2}}\\
&\quad + P_{F_2,3}e^{\chi_{F_2,3}} + P_{F_2,4}e^{\chi_{F_2,4}} + p_{F_2,1}e^{2\chi_{F_1,1}}\\
&\quad + p_{F_2,2}e^{2\chi_{F_1,2}} + p_{F_2,3}e^{2\chi_{F_1,3}} + p_{F_2,4}e^{2\chi_{F_1,4}}\\
&\quad + p_{F_2,5}e^{\chi_{F_1,1}+\chi_{F_1,2}} + p_{F_2,6}e^{\chi_{F_1,1}+\chi_{F_1,3}}\\
&\quad + p_{F_2,7}e^{\chi_{F_1,1}+\chi_{F_1,4}} + p_{F_2,8}e^{\chi_{F_1,2}+\chi_{F_1,3}}\\
&\quad + p_{F_2,9}e^{\chi_{F_1,2}+\chi_{F_1,4}}\\
&\quad + p_{F_2,10}e^{\chi_{F_1,3}+\chi_{F_1,4}}. \qquad (50b)
\end{aligned}$$

Third order FRFs $G_3(x,\omega,\omega,\omega)$ and $F_3(x,\omega,\omega,\omega)$

Following already described procedure for the first and second order FRFs, but collecting terms containing $(A/2)^3e^{3j\omega t}$ the third order FRFs at the distance x from the column inlet of both components ($G_3(x,\omega,\omega,\omega)$ and $F_3(x,\omega,\omega,\omega)$) as well as at the column outlet ($G_3(x=1,\omega,\omega,\omega) = G_3^*(\omega,\omega,\omega)$ and $F_3(x=1,\omega,\omega,\omega) = F_3^*(\omega,\omega,\omega)$) are derived. The third order FRFs $G_3(x,\omega,\omega,\omega)$ and $F_3(x,\omega,\omega,\omega)$ are proportional to the dominant term of the third harmonic in the output and only terms that contain $(A/2)^3e^{3j\omega t}$ are involved in their derivation (Weiner and Spina 1980).

The equations that define these third order FRFs are:

$$\begin{aligned}
&\frac{d^2G_3(x,\omega,\omega,\omega)}{dx^2} - 2N_{tp}\frac{dG_3(x,\omega,\omega,\omega)}{dx}\\
&\quad - 6N_{tp}j\omega(1+f_1\tilde{a}_{11})G_3(x,\omega,\omega,\omega)\\
&\quad - 6N_{tp}j\omega f_1\tilde{a}_{12}F_3(x,\omega,\omega,\omega) = R_{G_3}(x,\omega,\omega,\omega), \qquad (51a)
\end{aligned}$$

$$\begin{aligned}
&\frac{d^2F_3(x,\omega,\omega,\omega)}{dx^2} - 2N_{tp}\frac{dF_3(x,\omega,\omega,\omega)}{dx}\\
&\quad - 6N_{tp}j\omega(1+f_2\tilde{a}_{22})F_3(x,\omega,\omega,\omega)\\
&\quad - 6N_{tp}j\omega f_2\tilde{a}_{21}G_3(x,\omega,\omega,\omega) = R_{F_3}(x,\omega,\omega,\omega) \qquad (51b)
\end{aligned}$$

where $R_{G_3}(x,\omega,\omega,\omega)$ is:

$$\begin{aligned}
&R_{G_3}(x,\omega,\omega,\omega)\\
&\quad = 6N_{tp}j\omega f_1\{2\tilde{b}_{11}G_1(x,\omega)G_2(x,\omega,\omega) + 2\tilde{b}_{12}F_1(x,\omega)\\
&\qquad \times F_2(x,\omega,\omega) + \tilde{b}_{13}(G_1(x,\omega)F_2(x,\omega,\omega)\\
&\qquad + G_2(x,\omega,\omega)F_1(x,\omega)) + \tilde{c}_{11}G_1^3(x,\omega)\\
&\qquad + \tilde{c}_{12}F_1^3(x,\omega) + \tilde{c}_{13}G_1^2(x,\omega)F_1(x,\omega)\\
&\qquad + \tilde{c}_{14}G_1(x,\omega)F_1^2(x,\omega)\} \qquad (52a)
\end{aligned}$$

and $R_{F_3}(x,\omega,\omega,\omega)$:

$$\begin{aligned}
&R_{F_3}(x,\omega,\omega,\omega)\\
&\quad = 6N_{tp}j\omega f_2\{2\tilde{b}_{21}G_1(x,\omega)G_2(x,\omega,\omega) + 2\tilde{b}_{22}F_1(x,\omega)\\
&\qquad \times F_2(x,\omega,\omega) + \tilde{b}_{23}(G_1(x,\omega)F_2(x,\omega,\omega)\\
&\qquad + G_2(x,\omega,\omega)F_1(x,\omega)) + \tilde{c}_{21}G_1^3(x,\omega)\\
&\qquad + \tilde{c}_{22}F_1^3(x,\omega) + \tilde{c}_{23}G_1^2(x,\omega)F_1(x,\omega)\\
&\qquad + \tilde{c}_{24}G_1(x,\omega)F_1^2(x,\omega)\}. \qquad (53a)
\end{aligned}$$

The boundary conditions in the Volterra series form are:

$$\begin{aligned}
x=0:\quad & G_3(0,\omega,\omega,\omega) = \frac{1}{2N_{tp}}\cdot\left.\frac{dG_3(x,\omega,\omega,\omega)}{dx}\right|_{x=0};\\
& F_3(0,\omega,\omega,\omega) = \frac{1}{2N_{tp}}\cdot\left.\frac{dF_3(x,\omega,\omega,\omega)}{dx}\right|_{x=0} \qquad (54a)\\
x=1:\quad & \left.\frac{dG_3(x,\omega,\omega,\omega)}{dx}\right|_{x=1} = 0;\\
& \left.\frac{dF_3(x,\omega,\omega,\omega)}{dx}\right|_{x=1} = 0. \qquad (54b)
\end{aligned}$$

They are the same no matter if the concentration of only one or both components is varied at the inlet.

Combination of (51a) and (51b) yields:

$$\begin{aligned}
&\frac{d^4G_3(x,\omega,\omega,\omega)}{dx^4} - 4N_{tp}\frac{d^3G_3(x,\omega,\omega,\omega)}{dx^3}\\
&\quad + r_{G_3,1}\frac{d^2G_3(x,\omega,\omega,\omega)}{dx^2} + r_{G_3,2}\frac{dG_3(x,\omega,\omega,\omega)}{dx}\\
&\quad + r_{G_3,3}G_3(x,\omega,\omega,\omega)\\
&= 6N_{tp}j\omega f_1\tilde{a}_{12}R_{F_3}(x,\omega,\omega,\omega)\\
&\quad + \frac{d^2R_{G_3}(x,\omega,\omega,\omega)}{dx^2} - 2N_{tp}\frac{dR_{G_3}(x,\omega,\omega,\omega)}{dx}\\
&\quad - 6N_{tp}j\omega(1+f_2\tilde{a}_{22})R_{G_3}(x,\omega,\omega,\omega), \qquad (55a)
\end{aligned}$$

$$\begin{aligned}
&\frac{d^4F_3(x,\omega,\omega,\omega)}{dx^4} - 4N_{tp}\frac{d^3F_3(x,\omega,\omega,\omega)}{dx^3}\\
&\quad + r_{F_3,1}\frac{d^2F_3(x,\omega,\omega,\omega)}{dx^2} + r_{F_3,2}\frac{dF_3(x,\omega,\omega,\omega)}{dx}\\
&\quad + r_{F_3,3}F_3(x,\omega,\omega,\omega)\\
&= 6N_{tp}j\omega f_2\tilde{a}_{21}R_{G_3}(x,\omega,\omega,\omega)
\end{aligned}$$

$$
\begin{aligned}
&+\frac{d^2R_{F_3}(x,\omega,\omega,\omega)}{dx^2}-2N_{tp}\frac{dR_{F_3}(x,\omega,\omega,\omega)}{dx}\\
&-6N_{tp}j\omega(1+f_1\tilde{a}_{11})R_{F_3}(x,\omega,\omega,\omega) \qquad \text{(55b)}
\end{aligned}
$$

where coefficients $r_{G_3,i}$ and $r_{F_3,i}$ are given as:

$$
\begin{aligned}
r_{G_3,1}&=r_{F_3,1}=r_{G_3/F_3,1}\\
&=4N_{tp}^2-6N_{tp}j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}), \qquad \text{(56a)}\\
r_{G_3,2}&=r_{F_3,2}=r_{G_3/F_3,2}\\
&=12N_{tp}^2j\omega(2+f_1\tilde{a}_{11}+f_2\tilde{a}_{22}), \qquad \text{(56b)}\\
r_{G_3,3}&=r_{F_3,3}=r_{G_3/F_3,3}\\
&=36N_{tp}^2\omega^2(f_1f_2(\tilde{a}_{12}\tilde{a}_{21}-\tilde{a}_{11}\tilde{a}_{22})\\
&\quad -f_1\tilde{a}_{11}-f_2\tilde{a}_{22}-1). \qquad \text{(56c)}
\end{aligned}
$$

Equations (55a) and (55b) are linear, nonhomogeneous fourth-order ODEs with constant coefficients, as it is case for the second order FRF. Their solution similar is to the one for the second order FRF, but having the particular solution with more terms:

$$
\begin{aligned}
&G_3(x,\omega,\omega,\omega)\\
&=P_{G_3,1}e^{\chi_{G_3,1}x}+P_{G_3,2}e^{\chi_{G_3,2}x}\\
&\quad+P_{G_3,3}e^{\chi_{G_3,3}x}+P_{G_3,4}e^{\chi_{G_3,4}x}+p_{G_3,1}e^{3\chi_{G_1,1}x}\\
&\quad+p_{G_3,2}e^{3\chi_{G_1,2}x}p_{G_3,3}e^{3\chi_{G_1,3}x}+p_{G_3,4}e^{3\chi_{G_1,4}x}\\
&\quad+p_{G_3,5}e^{(\chi_{G_1,1}+\chi_{G_2,1})x}+p_{G_3,6}e^{(\chi_{G_1,1}+\chi_{G_2,2})x}\\
&\quad+p_{G_3,7}e^{(\chi_{G_1,1}+\chi_{G_2,3})x}+p_{G_3,8}e^{(\chi_{G_1,1}+\chi_{G_2,4})x}\\
&\quad+p_{G_3,9}e^{(\chi_{G_1,2}+\chi_{G_2,1})x}+p_{G_3,10}e^{(\chi_{G_1,2}+\chi_{G_2,2})x}\\
&\quad+p_{G_3,11}e^{(\chi_{G_1,2}+\chi_{G_2,3})x}+p_{G_3,12}e^{(\chi_{G_1,2}+\chi_{G_2,4})x}\\
&\quad+p_{G_3,13}e^{(\chi_{G_1,3}+\chi_{G_2,1})x}+p_{G_3,14}e^{(\chi_{G_1,3}+\chi_{G_2,2})x}\\
&\quad+p_{G_3,15}e^{(\chi_{G_1,3}+\chi_{G_2,3})x}+p_{G_3,16}e^{(\chi_{G_1,3}+\chi_{G_2,4})x}\\
&\quad+p_{G_3,17}e^{(\chi_{G_1,4}+\chi_{G_2,1})x}+p_{G_3,18}e^{(\chi_{G_1,4}+\chi_{G_2,2})x}\\
&\quad+p_{G_3,19}e^{(\chi_{G_1,4}+\chi_{G_2,3})x}+p_{G_3,20}e^{(\chi_{G_1,4}+\chi_{G_2,4})x}\\
&\quad+p_{G_3,21}e^{(2\chi_{G_1,1}+\chi_{G_1,2})x}+p_{G_3,22}e^{(2\chi_{G_1,1}+\chi_{G_1,3})x}\\
&\quad+p_{G_3,23}e^{(2\chi_{G_1,1}+\chi_{G_1,4})x}+p_{G_3,24}e^{(\chi_{G_1,1}+2\chi_{G_1,2})x}\\
&\quad+p_{G_3,25}e^{(2\chi_{G_1,2}+\chi_{G_1,3})x}+p_{G_3,26}e^{(2\chi_{G_1,2}+\chi_{G_1,4})x}\\
&\quad+p_{G_3,27}e^{(\chi_{G_1,1}+2\chi_{G_1,3})x}+p_{G_3,28}e^{(\chi_{G_1,2}+2\chi_{G_1,3})x}\\
&\quad+p_{G_3,29}e^{(2\chi_{G_1,3}+\chi_{G_1,4})x}+p_{G_3,30}e^{(\chi_{G_1,1}+2\chi_{G_1,4})x}\\
&\quad+p_{G_3,31}e^{(\chi_{G_1,2}+2\chi_{G_1,4})x}+p_{G_3,32}e^{(\chi_{G_1,3}+2\chi_{G_1,4})x}\\
&\quad+p_{G_3,33}e^{(\chi_{G_1,1}+\chi_{G_1,2}+\chi_{G_1,3})x}\\
&\quad+p_{G_3,34}e^{(\chi_{G_1,1}+\chi_{G_1,2}+\chi_{G_1,4})x}\\
&\quad+p_{G_3,35}e^{(\chi_{G_1,1}+\chi_{G_1,3}+\chi_{G_1,4})x}\\
&\quad+p_{G_3,36}e^{(\chi_{G_1,2}+\chi_{G_1,3}+\chi_{G_1,4})x}, \qquad \text{(57a)}
\end{aligned}
$$

$$
\begin{aligned}
&F_3(x,\omega,\omega,\omega)\\
&=P_{F_3,1}e^{\chi_{F_3,1}x}+P_{F_3,2}e^{\chi_{F_3,2}x}+P_{F_3,3}e^{\chi_{F_3,3}x}\\
&\quad+P_{F_3,4}e^{\chi_{F_3,4}x}+p_{F_3,1}e^{3\chi_{F_1,1}x}+p_{F_3,2}e^{3\chi_{F_1,2}x}\\
&\quad+p_{F_3,3}e^{3\chi_{F_1,3}x}+p_{F_3,4}e^{3\chi_{F_1,4}x}+p_{F_3,5}e^{(\chi_{F_1,1}+\chi_{F_2,1})x}\\
&\quad+p_{F_3,6}e^{(\chi_{F_1,1}+\chi_{F_2,2})x}+p_{F_3,7}e^{(\chi_{F_1,1}+\chi_{F_2,3})x}\\
&\quad+p_{F_3,8}e^{(\chi_{F_1,1}+\chi_{F_2,4})x}+p_{F_3,9}e^{(\chi_{F_1,2}+\chi_{F_2,1})x}\\
&\quad+p_{F_3,10}e^{(\chi_{F_1,2}+\chi_{F_2,2})x}+p_{F_3,11}e^{(\chi_{F_1,2}+\chi_{F_2,3})x}\\
&\quad+p_{F_3,12}e^{(\chi_{F_1,2}+\chi_{F_2,4})x}+p_{F_3,13}e^{(\chi_{F_1,3}+\chi_{F_2,1})x}\\
&\quad+p_{F_3,14}e^{(\chi_{F_1,3}+\chi_{F_2,2})x}+p_{F_3,15}e^{(\chi_{F_1,3}+\chi_{F_2,3})x}\\
&\quad+p_{F_3,16}e^{(\chi_{F_1,3}+\chi_{F_2,4})x}+p_{F_3,17}e^{(\chi_{F_1,4}+\chi_{F_2,1})x}\\
&\quad+p_{F_3,18}e^{(\chi_{F_1,4}+\chi_{F_2,2})x}+p_{F_3,19}e^{(\chi_{F_1,4}+\chi_{F_2,3})x}\\
&\quad+p_{F_3,20}e^{(\chi_{F_1,4}+\chi_{F_2,4})x}+p_{F_3,21}e^{(2\chi_{F_1,1}+\chi_{F_1,2})x}\\
&\quad+p_{F_3,22}e^{(2\chi_{F_1,1}+\chi_{F_1,3})x}+p_{F_3,23}e^{(2\chi_{F_1,1}+\chi_{F_1,4})x}\\
&\quad+p_{F_3,24}e^{(\chi_{F_1,1}+2\chi_{F_1,2})x}+p_{F_3,25}e^{(2\chi_{F_1,2}+\chi_{F_1,3})x}\\
&\quad+p_{F_3,26}e^{(2\chi_{F_1,2}+\chi_{F_1,4})x}+p_{F_3,27}e^{(\chi_{F_1,1}+2\chi_{F_1,3})x}\\
&\quad+p_{F_3,28}e^{(\chi_{F_1,2}+2\chi_{F_1,3})x}+p_{F_3,29}e^{(2\chi_{F_1,3}+\chi_{F_1,4})x}\\
&\quad+p_{F_3,30}e^{(\chi_{F_1,1}+2\chi_{F_1,4})x}+p_{F_3,31}e^{(\chi_{F_1,2}+2\chi_{F_1,4})x}\\
&\quad+p_{F_3,32}e^{(\chi_{F_1,3}+2\chi_{F_1,4})x}+p_{F_3,33}e^{(\chi_{F_1,1}+\chi_{F_1,2}+\chi_{F_1,3})x}\\
&\quad+p_{F_3,34}e^{(\chi_{F_1,1}+\chi_{F_1,2}+\chi_{F_1,4})x}\\
&\quad+p_{F_3,35}e^{(\chi_{F_1,1}+\chi_{F_1,3}+\chi_{F_1,4})x}\\
&\quad+p_{F_3,36}e^{(\chi_{F_1,2}+\chi_{F_1,3}+\chi_{F_1,4})x}. \qquad \text{(57b)}
\end{aligned}
$$

The characteristic equation that corresponds to the solution of the (55a) and (55b) is:

$$
\begin{aligned}
&\chi_{G_3/F_3}^4-4N_{tp}\chi_{G_3/F_3}^3+r_{G_3/F_3,1}\chi_{G_3/F_3}^2+r_{G_3/F_3,2}\chi_{G_3/F_3}\\
&\quad+r_{G_3/F_3,3}=0 \qquad \text{(58)}
\end{aligned}
$$

since the coefficients $r_{G_3,i}$ and $r_{F_3,i}$are equal, (56a–56c), then the solutions of the characteristic equation ($\chi_{G_3,i}$ and $\chi_{F_3,i}$) are also equal and can be denoted by $\chi_{G_3/F_3,i}$. By introducing the particular solutions of the corresponding third order FRFs into (55a) and (55b) the integration constants $p_{G_3,1}$ to $p_{G_3,36}$ and $p_{F_3,1}$ to $p_{F_3,36}$ are calculated.

Integration constants in (57a) are:

$$
\begin{aligned}
p_{G_3,i}^{num}&=(6N_{tp}j\omega)^2f_1f_2\tilde{a}_{12}(2\tilde{b}_{21}P_{G_1,i}p_{G_2,i}\\
&\quad+2\tilde{b}_{22}P_{F_1,i}p_{F_2,i}+\tilde{b}_{23}(P_{G_1,i}p_{F_2,i}+P_{F_1,i}p_{G_2,i})\\
&\quad+\tilde{c}_{21}P_{G_1,i}^3+\tilde{c}_{22}P_{F_1,i}^3+\tilde{c}_{23}P_{G_1,i}^2P_{F_1,i}\\
&\quad+\tilde{c}_{24}P_{G_1,i}P_{F_1,i}^2)+6N_{tp}j\omega f_1(9\chi_{G_1,i}^2-6N_{tp}\chi_{G_1,i}\\
&\quad-6N_{tp}j\omega(1+f_2\tilde{a}_{22}))\cdot(2\tilde{b}_{11}P_{G_1,i}p_{G_2,i}
\end{aligned}
$$

Table 6 Combination of indexes for $p_{G_3,5}$–$p_{G_3,20}$ and $p_{F_3,5}$–$p_{F_3,20}$

k	***i***	***j***	***k***	***i***	***j***
5	1	1	**13**	3	1
6	1	2	**14**	3	2
7	1	3	**15**	3	3
8	1	4	**16**	3	4
9	2	1	**17**	4	1
10	2	2	**18**	4	2
11	2	3	**19**	4	3
12	2	4	**20**	4	4

Table 7 Combination of indexes for $p_{G_3,21}$–$p_{G_3,32}$ and $p_{F_3,21}$–$p_{F_3,32}$

l	***i***	***j***	***k***	***l***	***i***	***j***	***k***
21	1	2	5	**27**	3	1	6
22	1	3	6	**28**	3	2	8
23	1	4	7	**29**	3	4	10
24	2	1	5	**30**	4	1	7
25	2	3	8	**31**	4	2	9
26	2	4	9	**32**	4	3	10

$$\begin{aligned}
&+2\tilde{b}_{12}P_{F_1,i}p_{F_2,i}+\tilde{b}_{13}(P_{G_1,i}p_{F_2,i} \qquad (59)\\
&+P_{F_1,i}p_{G_2,i})+\tilde{c}_{11}P_{G_1,i}^3+\tilde{c}_{12}P_{F_1,i}^3\\
&+\tilde{c}_{13}P_{G_1,i}^2P_{F_1,i}+\tilde{c}_{14}P_{G_1,i}P_{F_1,i}^2),\\
p_{G_3,i}^{den}&=(3\chi_{G_1,i})^4-4N_{tp}(3\chi_{G_1,i})^3+r_{G_3,1}(3\chi_{G_1,i})^2\\
&+3\chi_{G_1,i}r_{G_3,2}+r_{G_3,3},\\
p_{G_3,i}&=\frac{p_{G_3,i}^{num}}{p_{G_3,i}^{den}},\quad i=1,2,3,4,
\end{aligned}$$

$$\begin{aligned}
p_{G_3,k}^{num}&=(6N_{tp}j\omega)^2f_1f_2\tilde{a}_{12}(2\tilde{b}_{21}P_{G_1,i}P_{G_2,i}\\
&+2\tilde{b}_{22}P_{F_1,i}P_{F_2,i}+\tilde{b}_{23}(P_{G_1,i}P_{F_2,i}+P_{F_1,i}P_{G_2,i}))\\
&+6N_{tp}j\omega f_1((\chi_{G_1,i}+\chi_{G_2,j})^2\\
&-2N_{tp}(\chi_{G_1,i}+\chi_{G_2,j})-6N_{tp}j\omega(1+f_2\tilde{a}_{22}))\\
&\times(2\tilde{b}_{11}P_{G_1,i}P_{G_2,i}+2\tilde{b}_{12}P_{F_1,i}P_{F_2,i} \qquad (60)\\
&+\tilde{b}_{13}(P_{G_1,i}P_{F_2,i}+P_{F_1,i}P_{G_2,i}),\\
p_{G_3,k}^{den}&=(\chi_{G_1,i}+\chi_{G_2,j})^4-4N_{tp}(\chi_{G_1,i}+\chi_{G_2,j})^3\\
&+r_{G_3,1}(\chi_{G_1,i}+\chi_{G_2,j})^2+(\chi_{G_1,i}\\
&+\chi_{G_2,j})r_{G_3,2}+r_{G_3,3},\\
p_{G_3,k}&=\frac{p_{G_3,k}^{num}}{p_{G_3,k}^{den}},\quad i,j=1,2,3,4;\ k=5,6,\ldots,20.
\end{aligned}$$

Combination of subscripts is given in Table 6.

$$\begin{aligned}
p_{G_3,l}^{num}&=(6N_{tp}j\omega)^2f_1f_2\tilde{a}_{12}\{(2\tilde{b}_{21}(P_{G_1,i}p_{G_2,k}\\
&+P_{G_1,j}p_{G_2,i})+2\tilde{b}_{22}(P_{F_1,i}p_{F_2,k}+P_{F_1,j}p_{F_2,i})\\
&+\tilde{b}_{23}(P_{G_1,i}p_{F_2,k}+P_{G_1,j}p_{F_2,i}+P_{F_1,i}p_{G_2,k}\\
&+P_{F_1,j}p_{G_2,i})+3\tilde{c}_{21}P_{G_1,i}^2P_{G_1,j}+3\tilde{c}_{22}P_{F_1,i}^2P_{F_1,j}\\
&+\tilde{c}_{23}(2P_{G_1,i}P_{G_1,j}P_{F_1,i}+P_{G_1,i}^2P_{F_1,j})\\
&+\tilde{c}_{24}(2P_{G_1,i}P_{F_1,i}P_{F_1,j}+P_{G_1,j}P_{F_1,i}^2)\}\\
&+6N_{tp}j\omega f_1((2\chi_{G_1,i}+\chi_{G_1,j})^2\\
&-2N_{tp}(2\chi_{G_1,i}+\chi_{G_1,j})-6N_{tp}j\omega(1+f_2\tilde{a}_{22}))\\
&\times\{2\tilde{b}_{11}(P_{G_1,i}p_{G_2,k}+P_{G_1,j}p_{G_2,i})\\
&+2\tilde{b}_{12}(P_{F_1,i}p_{F_2,k}+P_{F_1,j}p_{F_2,i}) \qquad (61)\\
&+\tilde{b}_{13}(P_{G_1,i}p_{F_2,k}+P_{G_1,j}p_{F_2,i}+P_{F_1,i}p_{G_2,k}\\
&+P_{F_1,j}p_{G_2,i})+3\tilde{c}_{11}P_{G_1,i}^2P_{G_1,j}\\
&+3\tilde{c}_{12}P_{F_1,i}^2P_{F_1,j}+\tilde{c}_{13}(2P_{G_1,i}P_{G_1,j}P_{F_1,i}\\
&+P_{G_1,i}^2P_{F_1,j})+\tilde{c}_{14}(2P_{G_1,i}P_{F_1,i}P_{F_1,j}\\
&+P_{G_1,j}P_{F_1,i}^2)\},\\
p_{G_3,l}^{den}&=(2\chi_{G_1,i}+\chi_{G_1,j})^4-4N_{tp}(2\chi_{G_1,i}+\chi_{G_1,j})^3\\
&+r_{G_3,1}(2\chi_{G_1,i}+\chi_{G_1,j})^2\\
&+r_{G_3,2}(2\chi_{G_1,i}+\chi_{G_1,j})+r_{G_3,3},\\
p_{G_3,l}&=\frac{p_{G_3,l}^{num}}{p_{G_3,l}^{den}},\quad l=21,22,\ldots,32;\ i,j=1,2,3,4;\\
&\quad i\neq j;\ k=5,6,\ldots,10.
\end{aligned}$$

Combination of subscripts is given in Table 7.

$$\begin{aligned}
p_{G_3,h}^{num}&=(6N_{tp}j\omega)^2f_1f_2\tilde{a}_{12}\{2\tilde{b}_{21}\\
&\times(P_{G_1,i}p_{G_2,\alpha}+P_{G_1,j}p_{G_2,\beta}+P_{G_1,k}p_{G_2,\gamma})\\
&+2\tilde{b}_{22}(P_{F_1,i}p_{F_2,\alpha}+P_{F_1,j}p_{F_2,\beta}+P_{F_1,k}p_{F_2,\gamma})\\
&+\tilde{b}_{23}(P_{G_1,i}p_{F_2,\alpha}+P_{G_1,j}p_{F_2,\beta}+P_{G_1,k}p_{F_2,\gamma}\\
&+P_{F_1,i}p_{G_2,\alpha}+P_{F_1,j}p_{G_2,\beta}+P_{F_1,k}p_{G_2,\gamma})\\
&+6\tilde{c}_{21}P_{G_1,i}P_{G_1,j}P_{G_1,k}+6\tilde{c}_{22}P_{F_1,i}P_{F_1,j}P_{F_1,k}\\
&+2\tilde{c}_{23}(P_{G_1,i}P_{G_1,j}P_{F_1,k}+P_{G_1,i}P_{G_1,k}P_{F_1,j}\\
&+P_{G_1,j}P_{G_1,k}P_{F_1,i})+2\tilde{c}_{24}(P_{G_1,i}P_{F_1,j}P_{F_1,k}\\
&+P_{G_1,j}P_{F_1,i}P_{F_1,k}+P_{G_1,k}P_{F_1,i}P_{F_1,j})\}\\
&+6N_{tp}j\omega f_1((\chi_{G_1,i}+\chi_{G_1,j}+\chi_{G_1,k})^2\\
&-2N_{tp}(\chi_{G_1,i}+\chi_{G_1,j}+\chi_{G_1,k})\\
&-6N_{tp}j\omega(1+f_2\tilde{a}_{22}))
\end{aligned}$$

Table 8 Combination of indexes for $p_{G_3,33}$–$p_{G_3,36}$ and $p_{F_3,33}$–$p_{F_3,36}$

h	*i*	*j*	*k*	*α*	*β*	*γ*
33	1	2	3	8	6	5
34	1	2	4	9	7	5
35	1	3	4	10	7	6
36	2	3	4	10	9	8

$$\begin{aligned}
&\times\bigl\{2\tilde b_{11}(P_{G_1,i}p_{G_2,\alpha}+P_{G_1,j}p_{G_2,\beta}+P_{G_1,k}p_{G_2,\gamma})\\
&+2\tilde b_{12}(P_{F_1,i}p_{F_2,\alpha}+P_{F_1,j}p_{F_2,\beta}+P_{F_1,k}p_{F_2,\gamma})\\
&+\tilde b_{13}(P_{G_1,i}p_{F_2,\alpha}+P_{G_1,j}p_{F_2,\beta}+P_{G_1,k}p_{F_2,\gamma}\\
&+P_{F_1,i}p_{G_2,\alpha}+P_{F_1,j}p_{G_2,\beta}+P_{F_1,k}p_{G_2,\gamma})\\
&+6\tilde c_{11}P_{G_1,i}P_{G_1,j}P_{G_1,k}+6\tilde c_{12}P_{F_1,i}P_{F_1,j}P_{F_1,k}\\
&+2\tilde c_{13}(P_{G_1,i}P_{G_1,j}P_{F_1,k}+P_{G_1,i}P_{G_1,k}P_{F_1,j}\\
&+P_{G_1,j}P_{G_1,k}P_{F_1,i})+2\tilde c_{14}(P_{G_1,i}P_{F_1,j}P_{F_1,k}\\
&+P_{G_1,j}P_{F_1,i}P_{F_1,k}+P_{G_1,k}P_{F_1,i}P_{F_1,j})\bigr\},
\end{aligned}\tag{62a}$$

$$\begin{aligned}
p^{den}_{G_3,h}&=(\chi_{G_1,i}+\chi_{G_1,j}+\chi_{G_1,k})^4-4N_{tp}(\chi_{G_1,i}\\
&\quad+\chi_{G_1,j}+\chi_{G_1,k})^3\\
&\quad+r_{G_3,1}(\chi_{G_1,i}+\chi_{G_1,j}+\chi_{G_1,k})^2\\
&\quad+r_{G_3,2}(\chi_{G_1,i}+\chi_{G_1,j}+\chi_{G_1,k})+r_{G_3,3},
\end{aligned}\tag{62b}$$

$$p_{G_3,h}=\frac{p^{num}_{G_3,h}}{p^{den}_{G_3,h}},\quad h=33,34,35,36;$$

$$i=1,2;\ j=2,3;\ k=3,4;\ i\neq j\neq k;$$

$$\alpha=8,9,10;\ \beta=6,7,9;\ \gamma=5,6,8.$$

Combination of subscripts is given in Table 8.

Integration constants in (57b) are:

$$\begin{aligned}
p^{num}_{F_3,i}&=(6N_{tp}j\omega)^2f_1f_2\tilde a_{21}(2\tilde b_{11}P_{G_1,i}p_{G_2,i}\\
&\quad+2\tilde b_{12}P_{F_1,i}p_{F_2,i}+\tilde b_{13}(P_{G_1,i}p_{F_2,i}+P_{F_1,i}p_{G_2,i})\\
&\quad+\tilde c_{11}P^3_{G_1,i}+\tilde c_{12}P^3_{F_1,i}+\tilde c_{13}P^2_{G_1,i}P_{F_1,i}\\
&\quad+\tilde c_{14}P_{G_1,i}P^2_{F_1,i})+6N_{tp}j\omega f_2(9\chi^2_{F_1,i}-6N_{tp}\chi_{F_1,i}\\
&\quad-6N_{tp}j\omega(1+f_1\tilde a_{11}))\\
&\quad\times(2\tilde b_{21}P_{G_1,i}p_{G_2,i}+2\tilde b_{22}P_{F_1,i}p_{F_2,i}\\
&\quad+\tilde b_{23}(P_{G_1,i}p_{F_2,i}+P_{F_1,i}p_{G_2,i})+\tilde c_{21}P^3_{G_1,i}\\
&\quad+\tilde c_{22}P^3_{F_1,i}+\tilde c_{23}P^2_{G_1,i}P_{F_1,i}+\tilde c_{24}P_{G_1,i}P^2_{F_1,i}),\\
p^{den}_{F_3,i}&=(3\chi_{F_1,i})^4-4N_{tp}(3\chi_{F_1,i})^3+r_{F_3,1}(3\chi_{F_1,i})^2\\
&\quad+3\chi_{F_1,i}r_{F_3,2}+r_{F_3,3},\\
p_{F_3,i}&=\frac{p^{num}_{F_3,i}}{p^{den}_{F_3,i}},\quad i=1,2,3,4,
\end{aligned}\tag{63}$$

$$\begin{aligned}
p^{num}_{F_3,k}&=(6N_{tp}j\omega)^2f_1f_2\tilde a_{21}(2\tilde b_{11}P_{G_1,i}P_{G_2,j}\\
&\quad+2\tilde b_{12}P_{F_1,i}P_{F_2,j}+\tilde b_{13}(P_{G_1,i}P_{F_2,j}+P_{F_1,i}P_{G_2,j})\\
&\quad+6N_{tp}j\omega f_2((\chi_{F_1,i}+\chi_{F_2,j})^2\\
&\quad-2N_{tp}(\chi_{F_1,i}+\chi_{F_2,j})-6N_{tp}j\omega(1+f_1\tilde a_{11}))\\
&\quad\times(2\tilde b_{21}P_{G_1,i}P_{G_2,j}+2\tilde b_{22}P_{F_1,i}P_{F_2,j}\\
&\quad+\tilde b_{23}(P_{G_1,i}P_{F_2,j}+P_{F_1,i}P_{G_2,j})),\\
p^{den}_{F_3,k}&=(\chi_{F_1,i}+\chi_{F_2,j})^4-4N_{tp}(\chi_{F_1,i}+\chi_{F_2,j})^3\\
&\quad+r_{F_3,1}(\chi_{F_1,i}+\chi_{F_2,j})^2\\
&\quad+r_{F_3,2}(\chi_{F_1,i}+\chi_{F_2,j})+r_{F_3,3},\\
p_{F_3,k}&=\frac{p^{num}_{F_3,k}}{p^{den}_{F_3,k}},\quad i,j=1,2,3,4;\ k=5,6,\ldots,20.
\end{aligned}\tag{64}$$

Combination of subscripts is the same as for the p_{G_3}-constants and is given in Table 6.

$$\begin{aligned}
p^{num}_{F_3,l}&=(6N_{tp}j\omega)^2f_1f_2\tilde a_{21}\bigl\{(2\tilde b_{11}(P_{G_1,i}p_{G_2,k}+P_{G_1,j}p_{G_2,i})\\
&\quad+2\tilde b_{12}(P_{F_1,i}p_{F_2,k}+P_{F_1,j}p_{F_2,i})+\tilde b_{13}(P_{G_1,i}p_{F_2,k}\\
&\quad+P_{G_1,j}p_{F_2,i}+P_{F_1,i}p_{G_2,k}+P_{F_1,j}p_{G_2,i})\\
&\quad+3\tilde c_{11}P^2_{G_1,i}P_{G_1,j}+3\tilde c_{12}P^2_{F_1,i}P_{F_1,j}\\
&\quad+\tilde c_{13}(2P_{G_1,i}P_{G_1,j}P_{F_1,i}+P^2_{G_1,i}P_{F_1,j})\\
&\quad+\tilde c_{14}(2P_{G_1,i}P_{F_1,i}P_{F_1,j}+P_{G_1,j}P^2_{F_1,i})\bigr\}\\
&\quad+6N_{tp}j\omega f_2((2\chi_{F_1,i}+\chi_{F_1,j})^2\\
&\quad-2N_{tp}(2\chi_{F_1,i}+\chi_{F_1,j})-6N_{tp}j\omega(1+f_1\tilde a_{11}))\\
&\quad\times\bigl\{2\tilde b_{21}(P_{G_1,i}p_{G_2,k}+P_{G_1,j}p_{G_2,i})\\
&\quad+2\tilde b_{22}(P_{F_1,i}p_{F_2,k}+P_{F_1,j}p_{F_2,i})\\
&\quad+\tilde b_{23}(P_{G_1,i}p_{F_2,k}+P_{G_1,j}p_{F_2,i}\\
&\quad+P_{F_1,i}p_{G_2,k}+P_{F_1,j}p_{G_2,i})\\
&\quad+3\tilde c_{21}P^2_{G_1,i}P_{G_1,j}+3\tilde c_{22}P^2_{F_1,i}P_{F_1,j}\\
&\quad+\tilde c_{23}(2P_{G_1,i}P_{G_1,j}P_{F_1,i}+P^2_{G_1,i}P_{F_1,j})\\
&\quad+\tilde c_{24}(2P_{G_1,i}P_{F_1,i}P_{F_1,j}+P_{G_1,j}P^2_{F_1,i})\bigr\},\\
p^{den}_{F_3,l}&=(2\chi_{F_1,i}+\chi_{F_1,j})^4-4N_{tp}(2\chi_{F_1,i}+\chi_{F_1,j})^3\\
&\quad+r_{F_3,1}(2\chi_{F_1,i}+\chi_{F_1,j})^2\\
&\quad+r_{F_3,2}(2\chi_{F_1,i}+\chi_{F_1,j})+r_{F_3,3},\\
p_{F_3,l}&=\frac{p^{num}_{F_3,l}}{p^{den}_{F_3,l}},\quad l=21,22,\ldots,32;\ i,j=1,2,3,4;\\
&\quad i\neq j;\ k=5,6,\ldots,10.
\end{aligned}\tag{65}$$

Combination of subscripts is the same as for the p_{G_3}-constants and is given in Table 7.

$$\begin{aligned}
p^{num}_{F_3,h} = {} & (6N_{tp}j\omega)^2 f_1 f_2 \tilde{a}_{21} \\
& \times \{2\tilde{b}_{11}(P_{G_1,i}p_{G_2,\alpha} + P_{G_1,j}p_{G_2,\beta} + P_{G_1,k}p_{G_2,\gamma}) \\
& + 2\tilde{b}_{12}(P_{F_1,i}p_{F_2,\alpha} + P_{F_1,j}p_{F_2,\beta} + P_{F_1,k}p_{F_2,\gamma}) \\
& + \tilde{b}_{13}(P_{G_1,i}p_{F_2,\alpha} + P_{G_1,j}p_{F_2,\beta} \\
& + P_{G_1,k}p_{F_2,\gamma} + P_{F_1,i}p_{G_2,\alpha} + P_{F_1,j}p_{G_2,\beta} \\
& + P_{F_1,k}p_{G_2,\gamma}) \\
& + 6\tilde{c}_{11}P_{G_1,i}P_{G_1,j}P_{G_1,k} + 6\tilde{c}_{12}P_{F_1,i}P_{F_1,j}P_{F_1,k} \\
& + 2\tilde{c}_{13}(P_{G_1,i}P_{G_1,j}P_{F_1,k} + P_{G_1,i}P_{G_1,k}P_{F_1,j} \\
& + P_{G_1,j}P_{G_1,k}P_{F_1,i}) + 2\tilde{c}_{14}(P_{G_1,i}P_{F_1,j}P_{F_1,k} \\
& + P_{G_1,j}P_{F_1,i}P_{F_1,k} + P_{G_1,k}P_{F_1,i}P_{F_1,j})\} \\
& + 6N_{tp}j\omega f_2((\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k})^2 \\
& - 2N_{tp}(\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k}) \\
& - 6N_{tp}j\omega(1 + f_1\tilde{a}_{11})) \\
& \times \{2\tilde{b}_{21}(P_{G_1,i}p_{G_2,\alpha} + P_{G_1,j}p_{G_2,\beta} + P_{G_1,k}p_{G_2,\gamma}) \\
& + 2\tilde{b}_{22}(P_{F_1,i}p_{F_2,\alpha} + P_{F_1,j}p_{F_2,\beta} + P_{F_1,k}p_{F_2,\gamma}) \\
& + \tilde{b}_{23}(P_{G_1,i}p_{F_2,\alpha} + P_{G_1,j}p_{F_2,\beta} + P_{G_1,k}p_{F_2,\gamma} \\
& + P_{F_1,i}p_{G_2,\alpha} + P_{F_1,j}p_{G_2,\beta} + P_{F_1,k}p_{G_2,\gamma}) \\
& + 6\tilde{c}_{21}P_{G_1,i}P_{G_1,j}P_{G_1,k} + 6\tilde{c}_{22}P_{F_1,i}P_{F_1,j}P_{F_1,k} \\
& + 2\tilde{c}_{23}(P_{G_1,i}P_{G_1,j}P_{F_1,k} + P_{G_1,i}P_{G_1,k}P_{F_1,j} \\
& + P_{G_1,j}P_{G_1,k}P_{F_1,i}) + 2\tilde{c}_{24}(P_{G_1,i}P_{F_1,j}P_{F_1,k} \\
& + P_{G_1,j}P_{F_1,i}P_{F_1,k} + P_{G_1,k}P_{F_1,i}P_{F_1,j})\}, \qquad (66a)
\end{aligned}$$

$$\begin{aligned}
p^{den}_{F_3,h} = {} & (\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k})^4 \\
& - 4N_{tp}(\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k})^3 \\
& + r_{F_3,1}(\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k})^2 \\
& + r_{F_3,2}(\chi_{F_1,i} + \chi_{F_1,j} + \chi_{F_1,k}) + r_{F_3,3}, \qquad (66b)
\end{aligned}$$

$$\begin{aligned}
p_{F_3,h} = {} & \frac{p^{num}_{F_3,h}}{p^{den}_{F_3,h}}, \quad h = 33, 34, 35, 36;\ i = 1, 2; \\
& j = 2, 3;\ k = 3, 4;\ i \neq j \neq k; \\
& \alpha = 8, 9, 10;\ \beta = 6, 7, 9;\ \gamma = 5, 6, 8.
\end{aligned}$$

Combination of subscripts is the same as for the p_{G_3}-constants and is given in Table 8.

Correlations between the integration constants $P_{G_3,1}$ to $P_{G_3,4}$ and $P_{F_3,1}$ to $P_{F_3,4}$ are obtained in a similar way as for the constants that correspond to the second order FRF, whereby the $P_{F_3,i}$ constant can be expressed as a function of the $P_{G_3,i}$ constant in a similar way as P constants corresponding to the first and the second order FRFs ($P_{G_1,i}$, $P_{F_1,i}$, $P_{G_2,i}$ and $P_{F_2,i}$):

$$P_{F_3,i} = P_{G_3,i}\frac{\chi^2_{G_3,i} - 2N_{tp}\chi_{G_3,i} - 6N_{tp}j\omega(1 + f_1\tilde{a}_{11})}{6N_{tp}j\omega f_1\tilde{a}_{12}}, \quad i = 1, 2, 3, 4. \qquad (67)$$

The integration constants $P_{G_3,i}$ are calculated as a result of solving a system of four equations, that is obtained by introducing (57a), (57b) and (67) into (54a) and (54b). Their analytical expressions will not be given here, since they are rather cumbersome, as in the previous cases.

The third order FRFs for both components on the column scale are of the following general form:

$$\begin{aligned}
& G^*_3(\omega, \omega, \omega) \\
& = G_3(1, \omega, \omega, \omega) \\
& = P_{G_3,1}e^{\chi_{G_3,1}} + P_{G_3,2}e^{\chi_{G_3,2}} \\
& \quad + P_{G_3,3}e^{\chi_{G_3,3}} + P_{G_3,4}e^{\chi_{G_3,4}} + p_{G_3,1}e^{3\chi_{G_1,1}} \\
& \quad + p_{G_3,2}e^{3\chi_{G_1,2}} + p_{G_3,3}e^{3\chi_{G_1,3}} + p_{G_3,4}e^{3\chi_{G_1,4}} \\
& \quad + p_{G_3,5}e^{\chi_{G_1,1}+\chi_{G_2,1}} + p_{G_3,6}e^{\chi_{G_1,1}+\chi_{G_2,2}} \\
& \quad + p_{G_3,7}e^{\chi_{G_1,1}+\chi_{G_2,3}} + p_{G_3,8}e^{\chi_{G_1,1}+\chi_{G_2,4}} \\
& \quad + p_{G_3,9}e^{\chi_{G_1,2}+\chi_{G_2,1}} + p_{G_3,10}e^{\chi_{G_1,2}+\chi_{G_2,2}} \\
& \quad + p_{G_3,11}e^{\chi_{G_1,2}+\chi_{G_2,3}} + p_{G_3,12}e^{\chi_{G_1,2}+\chi_{G_2,4}} \\
& \quad + p_{G_3,13}e^{\chi_{G_1,3}+\chi_{G_2,1}} + p_{G_3,14}e^{\chi_{G_1,3}+\chi_{G_2,2}} \\
& \quad + p_{G_3,15}e^{\chi_{G_1,3}+\chi_{G_2,3}} + p_{G_3,16}e^{\chi_{G_1,3}+\chi_{G_2,4}} \\
& \quad + p_{G_3,17}e^{\chi_{G_1,4}+\chi_{G_2,1}} + p_{G_3,18}e^{\chi_{G_1,4}+\chi_{G_2,2}} \\
& \quad + p_{G_3,19}e^{\chi_{G_1,4}+\chi_{G_2,3}} + p_{G_3,20}e^{\chi_{G_1,4}+\chi_{G_2,4}} \\
& \quad + p_{G_3,21}e^{2\chi_{G_1,1}+\chi_{G_1,2}} + p_{G_3,22}e^{2\chi_{G_1,1}+\chi_{G_1,3}} \\
& \quad + p_{G_3,23}e^{2\chi_{G_1,1}+\chi_{G_1,4}} + p_{G_3,24}e^{\chi_{G_1,1}+2\chi_{G_1,2}} \\
& \quad + p_{G_3,25}e^{2\chi_{G_1,2}+\chi_{G_1,3}} + p_{G_3,26}e^{2\chi_{G_1,2}+\chi_{G_1,4}} \\
& \quad + p_{G_3,27}e^{\chi_{G_1,1}+2\chi_{G_1,3}} + p_{G_3,28}e^{\chi_{G_1,2}+2\chi_{G_1,3}} \\
& \quad + p_{G_3,29}e^{2\chi_{G_1,3}+\chi_{G_1,4}} + p_{G_3,30}e^{\chi_{G_1,1}+2\chi_{G_1,4}} \\
& \quad + p_{G_3,31}e^{\chi_{G_1,2}+2\chi_{G_1,4}} + p_{G_3,32}e^{\chi_{G_1,3}+2\chi_{G_1,4}} \\
& \quad + p_{G_3,33}e^{\chi_{G_1,1}+\chi_{G_1,2}+\chi_{G_1,3}} + p_{G_3,34}e^{\chi_{G_1,1}+\chi_{G_1,2}+\chi_{G_1,4}} \\
& \quad + p_{G_3,35}e^{\chi_{G_1,1}+\chi_{G_1,3}+\chi_{G_1,4}} \\
& \quad + p_{G_3,36}e^{\chi_{G_1,2}+\chi_{G_1,3}+\chi_{G_1,4}} \qquad (68a)
\end{aligned}$$

$$\begin{aligned}
& F^*_3(\omega, \omega, \omega) \\
& = F_3(1, \omega, \omega, \omega) \\
& = P_{F_3,1}e^{\chi_{F_3,1}} + P_{F_3,2}e^{\chi_{F_3,2}} + P_{F_3,3}e^{\chi_{F_3,3}} + P_{F_3,4}e^{\chi_{F_3,4}}
\end{aligned}$$

$$\begin{aligned}
&+ p_{F_3,1}e^{3\chi_{F_1,1}} + p_{F_3,2}e^{3\chi_{F_1,2}}\\
&+ p_{F_3,3}e^{3\chi_{F_1,3}} + p_{F_3,4}e^{3\chi_{F_1,4}} + p_{F_3,5}e^{\chi_{F_1,1}+\chi_{F_2,1}}\\
&+ p_{F_3,6}e^{\chi_{F_1,1}+\chi_{F_2,2}} + p_{F_3,7}e^{\chi_{F_1,1}+\chi_{F_2,3}}\\
&+ p_{F_3,8}e^{\chi_{F_1,1}+\chi_{F_2,4}} + p_{F_3,9}e^{\chi_{F_1,2}+\chi_{F_2,1}}\\
&+ p_{F_3,10}e^{\chi_{F_1,2}+\chi_{F_2,2}} + p_{F_3,11}e^{\chi_{F_1,2}+\chi_{F_2,3}}\\
&+ p_{F_3,12}e^{\chi_{F_1,2}+\chi_{F_2,4}} + p_{F_3,13}e^{\chi_{F_1,3}+\chi_{F_2,1}}\\
&+ p_{F_3,14}e^{\chi_{F_1,3}+\chi_{F_2,2}} + p_{F_3,15}e^{\chi_{F_1,3}+\chi_{F_2,3}}\\
&+ p_{F_3,16}e^{\chi_{F_1,3}+\chi_{F_2,4}} + p_{F_3,17}e^{\chi_{F_1,4}+\chi_{F_2,1}}\\
&+ p_{F_3,18}e^{\chi_{F_1,4}+\chi_{F_2,2}} + p_{F_3,19}e^{\chi_{F_1,4}+\chi_{F_2,3}}\\
&+ p_{F_3,20}e^{\chi_{F_1,4}+\chi_{F_2,4}} + p_{F_3,21}e^{2\chi_{F_1,1}+\chi_{F_1,2}}\\
&+ p_{F_3,22}e^{2\chi_{F_1,1}+\chi_{F_1,3}} + p_{F_3,23}e^{2\chi_{F_1,1}+\chi_{F_1,4}}\\
&+ p_{F_3,24}e^{\chi_{F_1,1}+2\chi_{F_1,2}} + p_{F_3,25}e^{2\chi_{F_1,2}+\chi_{F_1,3}}\\
&+ p_{F_3,26}e^{2\chi_{F_1,2}+\chi_{F_1,4}} + p_{F_3,27}e^{\chi_{F_1,1}+2\chi_{F_1,3}}\\
&+ p_{F_3,28}e^{\chi_{F_1,2}+2\chi_{F_1,3}} + p_{F_3,29}e^{2\chi_{F_1,3}+\chi_{F_1,4}}\\
&+ p_{F_3,30}e^{\chi_{F_1,1}+2\chi_{F_1,4}} + p_{F_3,31}e^{\chi_{F_1,2}+2\chi_{F_1,4}}\\
&+ p_{F_3,32}e^{\chi_{F_1,3}+2\chi_{F_1,4}} + p_{F_3,33}e^{\chi_{F_1,1}+\chi_{F_1,2}+\chi_{F_1,3}}\\
&+ p_{F_3,34}e^{\chi_{F_1,1}+\chi_{F_1,2}+\chi_{F_1,4}} + p_{F_3,35}e^{\chi_{F_1,1}+\chi_{F_1,3}+\chi_{F_1,4}}\\
&+ p_{F_3,36}e^{\chi_{F_1,2}+\chi_{F_1,3}+\chi_{F_1,4}}.
\end{aligned}\tag{68b}$$

References

Boniface, H.A., Ruthven, D.M.: Chromatographic adsorption with sinusoidal input. Chem. Eng. Sci. **40**(11), 2053–2061 (1985)

Dankwerts, P.V.: Continuous flow systems—distribution of residence times. Chem. Eng. Sci. **2**(1), 1–13 (1953)

Douglas, J.M.: Process Dynamics and Control. Prentice Hall, Englewood Cliffs (1972)

Gritti, F., Guiochon, G.: Band splitting in overloaded isocratic elution chromatography. II: new competitive adsorption isotherms. J. Chromatogr. A **1008**, 23–41 (2003)

Grzegorczyk, D.S., Carta, G.: Frequency response of liquid-phase adsorption on polymeric adsorbents. Chem. Eng. Sci. **52**(10), 1589–1608 (1997)

Guiochon, G., Shirazi, S.G., Katti, A.M.: Fundamentals of Preparative and Nonlinear Chromatography. Academic Press, Boston (1994)

Ilić, M., Petkovska, M., Seidel-Morgenstern, A.: Nonlinear frequency response functions of a chromatographic column—a critical evaluation of their potential for estimation of single solute adsorption isotherms. Chem. Eng. Sci. **62**, 1269–1281 (2007a)

Ilić, M., Petkovska, M., Seidel-Morgenstern, A.: Nonlinear frequency response method for estimation of single solute adsorption isotherms. Part I. Theoretical basis and simulations. Chem. Eng. Sci. **62**, 4379–4393 (2007b)

Ilić, M., Petkovska, M., Seidel-Morgenstern, A.: Nonlinear frequency response method for estimation of single solute adsorption isotherms, part II: experimental study. Chem. Eng. Sci. **62**, 4394–4408 (2007c)

Lang, Z.Q., Billings, S.A.: Energy transfer properties of non-linear systems in the frequency domain. Int. J. Control **78**(5), 345–362 (2005)

Naphtali, L.M., Polinski, L.M.: A novel technique for characterisation of adsorption rates on heterogeneous surfaces. J. Phys. Chem. **67**, 369–375 (1963)

Park, I.S., Petkovska, M., Do, D.D.: Frequency response of an adsorber with modulation of the inlet molar flow rate, I: semi-batch adsorber. Chem. Eng. Sci. **53**, 819–832 (1998a)

Park, I.S., Petkovska, M., Do, D.D.: Frequency response of an adsorber with modulation of the inlet molar flow rate, II: a continuous flow adsorber. Chem. Eng. Sci. **53**, 833–843 (1998b)

Park, I.S., Kwak, C., Hwang, Y.G.: Frequency response of continuous-flow adsorber for multicomponent system. Korean J. Chem. Eng. **17**, 704–711 (2000)

Petkovska, M.: Nonlinear frequency response method for investigation of equilibria and kinetics. In: Spasic, A.M., Hsu, J.P. (eds.) Adsorption Systems in Finely Dispersed Particles: Micro, Nano- and Atto-Engineering, pp. 283–327. CRC Press, Boca Raton (2005)

Petkovska, M., Do, D.D.: Use of higher order FRFs for identification of nonlinear adsorption kinetics: single mechanisms under isothermal conditions. Nonlinear Dyn. **21**, 353–376 (2000)

Petkovska, M., Petkovska, L.T.: Use of nonlinear frequency response for discriminating adsorption kinetics mechanisms resulting with bimodal characteristic functions. Adsorption **9**, 133–142 (2003)

Petkovska, M., Seidel-Morgenstern, A.: Nonlinear frequency response of a chromatographic column, part I: application to estimation of adsorption isotherms with inflection points. Chem. Eng. Commun. **192**, 1300–1333 (2005)

Rees, L.V.C., Song, L.: Frequency response methods for the characterization of microporous solids. In: Kanellopoulos, N.K. (ed.) Recent Advances in Gas Separation by Microporous Ceramic Membranes, pp. 139–186. Elsevier, Amsterdam (2000)

Rugh, W.J.: Nonlinear System Theory, The Volterra and Wiener Approach. John Hopkins University Press, Baltimore (1981)

Ruthven, D.M.: Principles of Adsorption and Adsorption Processes. Wiley, New York (1984)

Seidel-Morgenstern, A.: Experimental determination of single solute and competitive adsorption isotherms. J. Chromatogr. A **1037**, 255–272 (2004)

Sun, L.M., Zhong, G.M., Gray, P.G., Meunier, F.: Frequency response analysis for multicomponent diffusion in adsorbents. J. Chem. Soc. Faraday Trans. **90**(2), 369–376 (1994)

Sward, B.K., LeVan, M.D.: Frequency response method for measuring mass transfer rates in adsorbents via pressure modulation. Adsorption **9**, 37–54 (2003)

Wang, Y., LeVan, M.D.: Investigation of mixture diffusion in nanoporous adsorbents via the pressure-swing frequency response method, 1: theoretical treatment. Ind. Eng. Chem. Res. **44**, 3692–3701 (2005a)

Wang, Y., LeVan, M.D.: Investigation of mixture diffusion in nanoporous adsorbents via the pressure-swing frequency response method. 2: oxygen and nitrogen in a carbon molecular sieve. Ind. Eng. Chem. Res. **44**, 4745–4752 (2005b)

Wang, Y., Sward, B.K., LeVan, M.D.: New frequency response method for measuring adsorption rates via pressure modulation: application to oxygen and nitrogen in a carbon molecular sieve. Ind. Eng. Chem. Res. **42**, 4213–4222 (2003)

Weiner, D.D., Spina, J.F.: Sinusoidal Analysis and Modeling of Weakly Nonlinear Circuits. Reinhold, New York (1980)

Worden, K., Tomlinson, G.R.: Nonlinearity in Structural Dynamics. Institute of Physics Publishing, Bristol (2001)

Yasuda, Y., Yamada, Y., Matsuua, I.: New Developments in Zeolite Science and Technology. Elsevier, New York (1986)