

# On transfer function formalism for chemical reactor monitoring by continuous flow techniques

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Mathematical expressions for the response of a flow-through system for reactor monitoring have been obtained considering the transfer function formalism, where the output of a linear system to an arbitrary input signal could be known by means of the transfer function of this linear system. A transfer function without and with a pseudo-first order chemical reaction based on an axial dispersion model is proposed. These transfer functions allow the description of a great variety of situations as the dynamic response of the system equations against impulse, step and pulse perturbations. Two empirical parameters related with the diffusion coefficient of the solute and geometrical magnitudes of the flowing system are proposed. The model has been checked experimentally studying the dispersion of different non-reacting dye solutions and the kinetics of phenolphthalein decolouration in alkaline media.

**KEY WORDS:** dispersion model, diffusion, continuous flow analysis, FIA modelling, residence time distribution function

## 1. Introduction

One purpose of chemical engineering is the optimisation of a chemical reaction in an industrial scale. That implies an optimum design of the reactor based on a set of economical and physicochemical restrictions imposed by the system under study. Therefore, the knowledge of accurate and reliable kinetic data obtained in the laboratory is fundamental for this purpose. Factors as the laboratory reactor configuration, the sampling procedure and the analysis of product composition should be considered as a part of the experimental work in order to understand the observations done in these kinetic studies [1, 2].

Because of the kinetic character of this kind of experiments, the modelling of the measuring instrument together with the reactor model is highly recommended when the time response of the sensor is of the same order of magnitude

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as the process which we want to measure. The measurement step implies generally the sampling and acquisition of physical quantities, like pressure or temperature, with chemical ones, like product composition and concentrations. Thus, analytical methods are always linked with chemical engineering to monitor and control the industrial processes and the fastest available analytic method will be the preferred when different methods are applicable. Some of them allow knowing the concentration of the substance of interest *in situ*, in the reactor, but the sampling of the reactor and the analysis of the sample *ex situ* is a more common practice.

From the chemical engineering point of view, flow injection analysis (FIA) is an attractive analytical method because it enables relatively fast sampling and fast chemical analysis [3,4]. However, the main limitation of this technique is the physical phenomena involved in FIA: the dispersion of the solute in a fluid flowing through a tube. A basic FIA system is composed by a more or less complex tubing network, a fluid impulsion device, e.g. a peristaltic pump, and a measuring or detection cell. Each of these components contributes to physical dispersion and then, to the observed response of the system [5]. Although FIA is a specific technique developed in the chemical analysis context, the theoretical concepts used for its mathematical development are shared with chemical engineering.

The proposed theoretical models to explain the FIA dispersion phenomenon, can be grouped in three different categories: (i) diffusion–convection models, (ii) tank-in-series models, and (iii) semiempirical models.

The first group tackles with the problem of solving the continuity equation for the flow of a solute in a conduction. Depending on the geometrical definition of the problem, the continuity equation leads to different partial differential equations. The most simple and intuitive case is to consider the dispersion of a soluble substance in a fluid flowing in a tube as an effect of the combination of a diffusive and a convective mass transport. This problem was early treated by Taylor [6,7] and Aris [8] and has recently been generalised by Westerterp et al. [9]. Although the partial differential equation governing the diffusion–convection process could be written in different ways to account with varied phenomena [10], all these models agree with the fact that the radial diffusion of the solute contributes significantly to the dispersion of the sample in the conduction. Taylor's equation summarises this fact and has mainly been used to calculate diffusion coefficients of soluble substances [6,11,12].

The second group of theoretical models has been developed borrowing concepts from chemical engineering which deal with non-ideal flow in chemical reactors [13,14]. In this case, the FIA manifold is considered as a series of ideal continuous stirred tank reactors that causes the dispersion of the solute from one reactor to the next. The advantage of this model is its simplicity [15,16] but the obtained parameters characterising the dispersion are complex to interpret and use because of their statistical nature.

Finally, the third group of FIA models are based on experimental data [5], numerical simulations derived from resolution of the diffusion–convection partial differential equations [17, 18] or from simulation of random processes [19]. These models provide phenomenological equations that relate the calculated magnitudes as the dispersion or the time of residence to magnitudes as the tube diameter, its length, the diffusion coefficient of the solute, the temperature, etc., which can be modified by the user in the computational program. An empirical confirmation of these expressions is not always possible because the phenomena involved in an experimental setup implies the interrelation of various physical properties and no one can be modified without the perturbation of the rest of the parameters. Thus, the generalisation of these models is in fact cumbersome to be implemented for reactor monitoring and then should be considered carefully.

This work deals with the modelling and characterisation of flow injection systems for chemical reactor monitoring. The approach used here is the definition of a transfer function describing the dispersion process and the suggestion of an experimental and mathematical procedure to characterise it. Any physical system that can be described by a linear differential equation with all their values initially set to zero, can be modelled through a transfer function [20, 21]. If we suppose a system which is perturbed by a signal  $S(t)$ , it will respond to this perturbation giving the response  $R(t)$ . Considering the convolution theorem, both signals  $S(t)$  and  $R(t)$  or their Laplace transform,  $s(p)$  and  $r(p)$  respectively, are related with the transfer function of the system,  $h(p)$  through  $r(p) = s(p) \cdot h(p)$ . The transfer function proposed in this work defines two dispersion parameters that should be evaluated empirically in order to characterise the flowing system. If different dynamic processes are supposed in the reactor, the dynamic equation of the measured response as a function of the dispersion parameters can be calculated out from the transfer function of the system. Simple cases as the step and pulse perturbations will be shown in this paper with special attention on the determination of the dispersion parameters. Other cases such as the effect of the measuring-cell volume, first order kinetics and gas–liquid mass transfer will also be considered in this work. The aim of this work is to show the advantages of the transfer function formalism against other methodologies for obtaining analytical expressions of the response and for the interpretation of flow injection and continuous analysis systems. Experimental results for non-reacting and reacting systems agree with the theoretical predictions obtained by this way.

## 2. Transfer function for mass dispersion in continuous flow systems without chemical reactions

The monitoring of a chemical reactor using a flow injection system implies to set up the equipment depicted in figure 1. A continuous flow of solution

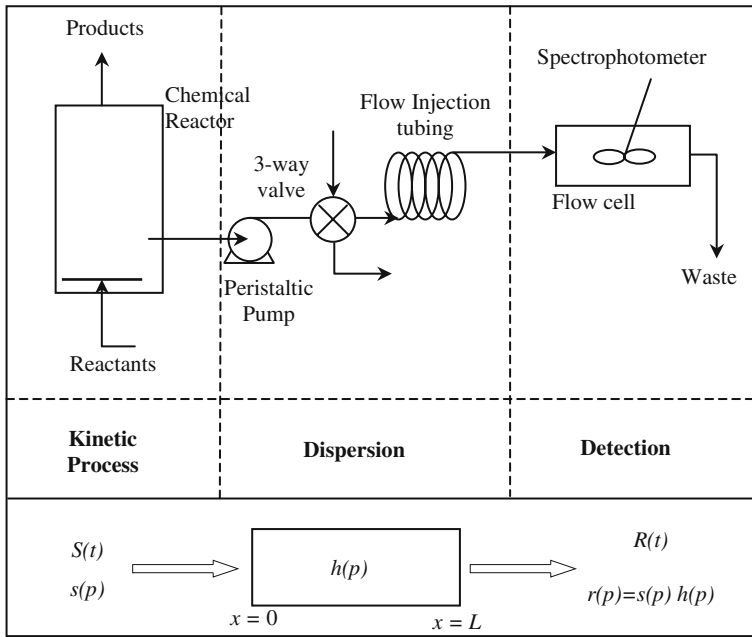


Figure 1. Experimental setup for the monitoring of a kinetic process in a chemical reactor by Flow Injection techniques. The measured response  $R(t)$  at the output is the result of the dispersion of the input signal,  $S(t)$ . This dispersion can be represented by the transfer function  $h(p)$  in the Laplace domain.  $S(t)$  can be any time-varying concentration perturbation caused by any kinetic process in the reactor. In the scheme, a gas-liquid mass transfer process has been considered.

from the reactor to the detector is impelled by a peristaltic pump. If the substance of interest is coloured or absorbs light in the UV region, i.e. the textile dyes or the ozone respectively, its evolution in the reactor can be followed by spectrophotometry. Experimentally it has been observed that if the FIA tube is initially absent of coloured substance and in the reactor the concentration of this substance remains constant, the observed response in the detector looks as a S-shaped (sigmoidal) curve as it is shown in figure 2, when a solute step is applied. The shape of this response differs from which is theoretically expected for a plug-flow model without chemical reaction, so the observed response should be attributed to the dispersion phenomena in the conduction.

In order to state the problem, consider the equation for mass transport of a solute flowing through a cylindrical pipe in laminar regime [6, 8]:

$$\frac{\partial C}{\partial t} = D_m \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2} \right) + u_0 \left( 1 - \frac{r^2}{R^2} \right) \frac{\partial C}{\partial x} \quad (1)$$

where  $r$  and  $x$  are the radial and axial coordinate respectively,  $R$  the tube radius,  $u_0$  the maximum flow rate in the center of the conduction and  $D_m$  is the molecular diffusion coefficient. The laminar regime is ensured in narrow tubes as

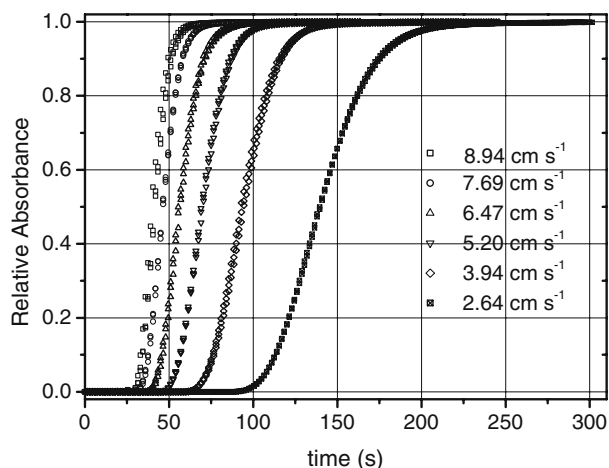


Figure 2. Concentration response of the flowing system against a step perturbation of Tartrazine dye solutions. Each curve is recorded in triplicate at different flow velocity.  $T = 293\text{ K}$ ,  $[\text{Tartrazine}] = 4.86 \times 10^{-5}\text{ M}$ ,  $L = 3\text{ m}$ , cell-flow volume =  $80\ \mu\text{l}$ ,  $\lambda = 427\text{ nm}$ .

those used in flow injection systems, then this hypothesis will be assumed in the following. Because the axial length in a flow system is several orders of magnitude higher than the tube radius, this equation is commonly reduced to the one-dimensional dispersion–convection equation [3, 10, 22, 23]. A more formal approach based on the method-of-moments reduces the microcontinuum transport equation (1) to a macrocontinuum one-dimensional transport equation which is, on the other hand, the basic methodology of macrotransport theory [8, 24]:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \quad (2)$$

Here  $C$  should be understood as the area-average concentration,  $D_a$  the macro-scale convection dispersivity coefficient which accounts for the radial and axial dispersion of the solute in the tube and  $u$  is defined as the area-average axial velocity of the fluid in the tube. This equation accounts for the dispersion phenomena in a circular tube without chemical reaction, but because the chemical reactions usually happen uniformly, it is common to add to this equation a kinetic term that does not modify substantially the results as it will be shown later. The diffusion coefficient  $D_m$  of equation (1) has been changed here to the dispersivity coefficient  $D_a$  because the simplification of the differential equation involves a change on the interpretation of the constants defining the physical problem [6, 8]. For circular tubes, the dispersivity coefficient is given by [6, 8, 24]:

$$D_a = D_m + \frac{u^2 R^2}{48 D_m} \quad (3)$$

where  $D_m$  is the molecular diffusion coefficient of the solute and  $R$  the inner radius of the dispersion tube.

Considering that the concentration in eq. (2) should be always bounded, a general solution can be calculated out applying the Laplace transform with initial conditions set to zero,  $C(x, t = 0) = 0$ :

$$c(x, p) = C_2(p) \exp\left(\frac{u x}{2 D_a}\right) \exp\left[\frac{-x}{D_a^{1/2}} \left(p + \frac{u^2}{4 D_a}\right)^{1/2}\right] \quad (4)$$

where  $c(x, p)$  is the Laplace transform of the concentration and  $C_2(p)$  is a constant to be evaluated from the boundary conditions. From here, references concerning flow injection systems deals with the application of different boundary conditions to obtain the temporal response of the system at  $x = L$  [22, 23]. Although this procedure has effectively been proved, it has the inconvenience that is not general for every physical system and in presence of chemical reactions can lead to complex analysis as well.

In the following, the concentration should be visualised as a perturbation of the flowing system applied at  $x = 0$  and a response read at  $x = L$ . The transfer function of a linear system with initial conditions set to zero is defined as the ratio between the system output and the perturbation input in the Laplace domain. Then, considering that at the beginning of the dispersion tube an arbitrary perturbation  $C(0, t)$  is applied, from equation (4) the transfer function for the dispersion phenomenon,  $h(p)$ , is deduced:

$$h(p) = \frac{c(L, p)}{c(0, p)} = \exp\left[\alpha\beta - \alpha(p + \beta^2)^{1/2}\right] \quad (5)$$

with  $\alpha = L/D_a^{1/2}$  and  $\beta = u/2D_a^{1/2}$ , which defines two dispersion parameters which should be obtained with experiments. Formally, the only unknown parameter of the system is the dispersivity coefficient, but because equation (2) is an approximation of equation (1) it is more convenient to define and maintain these two dispersion parameters for the full characterisation of the system, analysing subsequently the behaviour of these parameters for different operating conditions.

The physical meaning of  $\alpha$  and  $\beta$  cannot be precisely defined by dimensional analysis but few reasons suggest that these parameters could be considered as empirical coefficients to be calculated out from the experiments. First, the differential equation (2) from which the transfer function has been obtained does not result from a rigorous deduction of the original one (equation (1)). Then, these parameters collect some of the information of the original differential equation lost in the simplification step. Second, along the flow injection manifold there could be pipe fittings or elements that modifies the velocity profile in the tube and then, the magnitude  $u$  expressed in equation (2) accounts for the average of a distributed property. And third, the presence of these pipe

fittings along the tube can increase the true length of the conduction in some quantity, leading to an effective length of the conduction, that only can be evaluated with an experiment. Thus, the use of the dispersion transfer function makes advisable to consider the dispersion parameters  $\alpha$  and  $\beta$  as fit parameters to be calculated out from experimental data in order to characterise the flow injection system. Although the physical meaning of these two parameters is not trivial, from a phenomenological point of view the parameter  $\alpha$  is related with the time lag of the signal, increasing this delay as  $\alpha$  does (see figure 2). On the other hand, the parameter  $\beta$  is mainly related with the dispersion of the solute in the tube, decreasing the slope in the inflexion point as  $\beta$  increases. That means that as  $\beta$  increases, the spread of the solute along the tube is greater, as it could be deduced from figure 2 for slow fluid velocities.

The deduction of the transfer function (5) simplifies appreciably the procedure for the evaluation of the time-dependent concentration curves for complex systems. In the next section the concentration–time curves for few common perturbations and other physical situation without chemical reaction will be deduced. Later, the chemical reaction problem using the same formalism will be developed.

### 2.1. Step and pulse concentration input

The simplest way to carry out a dispersion experiment is by using the classical manifold for FIA technique switching between the carrier and the solution until a steady state has been reached. In these circumstances, the solution is injected through the dispersion tube in which initially the solute was absent. The applied perturbation can be written as

$$C(x = 0, t) = C_0 U(t) \quad (6)$$

where  $U(t)$  is the unit step or Heaviside function. Combining the Laplace transform of this function with equation (5), the response of the system is

$$C(L, t) = L^{-1} \left\{ C_0 \frac{1}{p} h(p) \right\} = C_0 \frac{\alpha}{2\pi^{1/2}} \int_0^t \theta^{-3/2} \exp \left[ -\frac{(\alpha - 2\beta\theta)^2}{4\theta} \right] d\theta \quad (7)$$

where  $L^{-1}$  is the inverse Laplace transform operator. If we define the new variables

$$y = \frac{\alpha + 2\beta\theta}{2\theta^{1/2}} \quad (8)$$

$$z = \frac{\alpha - 2\beta\theta}{2\theta^{1/2}} \quad (9)$$

the equation (7) can be rewritten as

$$C(L, t) = \frac{1}{2} C_0 \left\{ \operatorname{Erfc} \left( \frac{\alpha - 2\beta t}{2t^{1/2}} \right) + \exp(2\alpha\beta) \operatorname{Erfc} \left( \frac{\alpha + 2\beta t}{2t^{1/2}} \right) \right\} \quad (10)$$

where  $\operatorname{Erfc}(x)$  is the complementary error function [25]. For convenience let us define the new function  $F_S(t)$ , which represents the response of a unit step perturbation for a pure dispersion process:

$$F_S(t) = \frac{1}{2} \left\{ \operatorname{Erfc} \left( \frac{\alpha - 2\beta t}{2t^{1/2}} \right) + \exp(2\alpha\beta) \operatorname{Erfc} \left( \frac{\alpha + 2\beta t}{2t^{1/2}} \right) \right\} \quad (11)$$

There are accurate and fast algorithms which calculate the error function in equation (11) more efficiently than the particular integral defined in (7). Thus, this last function is advantageous in order to calculate the parameters  $\alpha$  and  $\beta$  from experimental data and was used to obtain the results shown below.

On the other hand, classical flow injection analysis (FIA) consists on the transport of a small sample volume injected into a carrier stream, flowing towards a chemical detector [3, 4]. This situation is similar to consider a pulse of concentration of duration  $\tau$ . It is important to insist here that in classical FIA the perturbation is similar to a pulse and the differences concern about the boundary conditions of the problem. So, only a pure pulse perturbation will be treated here.

Using the Heaviside function, the pulse perturbation can be written as:

$$C(0, t) = C_0 \{U(t) - U(t - \tau)\} \quad (12)$$

where  $\tau$  is the duration of the pulse. Using the properties of the Laplace transform, the convolution theorem and considering the definition of  $F_S(t)$  (equation (11)), it could be demonstrated that the response of the system is:

$$C(L, t) = C_0 \cdot \begin{cases} F_S(t), & t < \tau \\ F_S(t) - F_S(t - \tau), & t \geq \tau \end{cases} \quad (13)$$

This function has a maximum which generally is used in analytical chemistry as the measured magnitude in FIA. In this scientific context, the ratio between the input concentration and the concentration at the maximum is called "dispersion", which depends on the liquid flow, the tube length and the dispersion coefficients in a complex way [3, 4].

## 2.2. Effect of the volume of the cell

Flow Injection Analysis is the result of the combination of a classical analytical method with a pumping and an injection system which allows the continuous measuring of the analyte in a flowing cell. Electrochemical and spectroscopic techniques are common methods used in the detection step [3, 26]. In order to enhance the detection limit of the analytical method, it is a common practice in FIA to use flowing cells of large volume, in comparison of the flow



rate in the tube, fitted to the flow injection system manifold. This volume perturbs the interpretation of the measured response because the reading is the result of an average property measured in the whole volume of the cell. A first approach to analyse the influence of the measuring cell volume is to consider it as a continuous stirred tank (CST) coupled with the flow injection system.

From the mass balance equation of a CST it can be demonstrated that if the substance to be measured is initially absent in the tank, the transfer function which describes the response of this system is

$$h_{\text{CST}}(p) = \frac{1}{\tau_v p + 1} \quad (14)$$

where  $\tau_v$  is the hydraulic retention time of the tank. Because the dispersion through the FIA manifold and the mixing in the measuring cell are two successive steps, the transfer function for the whole process is the product of the two independent transfer functions:

$$f(p) = \frac{1}{\tau_v p + 1} \exp\left[\alpha\beta - \alpha(p + \beta^2)^{1/2}\right] \quad (15)$$

Let us consider now that the applied perturbation in the FIA system is a step concentration described by equation (6). In this case the measured response of the system will be written as

$$C(L, t) = C_0 \left( F_S(t) - \frac{1}{2} \exp\left[\alpha(\beta - m) - \frac{t}{\tau_v}\right] \times \left\{ \text{Erfc}\left(\frac{\alpha - 2mt}{2t^{1/2}}\right) + \exp(2\alpha m) \text{Erfc}\left(\frac{\alpha + 2mt}{2t^{1/2}}\right) \right\} \right) \quad (16)$$

where  $m = \sqrt{\beta^2 - \tau_v^{-1}}$ . As the retention time  $\tau_v$  decreases, the measured response approaches the ideal dispersion response described by equation (10). Conversely, as the retention time increases the response vanishes as a result of the dilution effect in the flow cell. Thus, according to the knowledge about the FIA techniques, the flow cell used in continuous monitoring of chemical reactors should be the smallest possible to reduce the distortion of experimental data.

### 2.3. An academic example: the gas-liquid mass transfer

Finally, let us consider now the monitoring of a time-dependent process without chemical reaction such as a gas-liquid mass transfer process. This problem will be considered here just from a theoretical point of view in order to show the versatility of the transfer function formalism for continuous flow techniques. Suppose we have a gas such as the ozone, which absorbs light in the ultraviolet region with its maximum absorbance at 254 nm [27, 28, 29]. This property allows

to set up a flow injection system such as depicted on figure 1 for the determination of this gas dissolved in water [30]. Ozone is a strong oxidising agent useful for the treatment of organic compounds present in wastewater resistant to conventional wastewater treatment processes. The effectiveness of ozonation process depends, among others, on the gas-liquid mass transfer coefficient, which represents the transfer rate of the ozone gas to the solution [27].

Several simple macroscopic models for the gas-liquid transfer process predict a concentration-time evolution in the liquid phase as a saturation curve:

$$C(t) = C_{\text{sat}} (1 - \exp(-k_L a \cdot t)) \quad (17)$$

where  $C_{\text{sat}}$  is the saturation concentration and  $k_L a$  is the mass transfer coefficient [27, 31]. This parameter can only be characterised through dynamic experiments because the progressive character of the gas dissolution process, then the FIA could be a good analytical method to follow the ozone concentration in the reactor. However, the main difficulty of this method is the interpretation of the experimental data due to the dispersion phenomenon. Combining the transfer function of the dispersion process (equation (5)) and the Laplace transform of the saturation curve for the dissolution of a gas in water (equation (17)), after Laplace inversion, the response read in the detector can be written as

$$C(L, t) = C_{\text{sat}} \left( F_S(t) - \frac{1}{2} \exp[\alpha(\beta - n) - k_L a \cdot t] \times \left\{ \text{Erfc} \left( \frac{\alpha - 2nt}{2t^{1/2}} \right) + \exp(2\alpha n) \text{Erfc} \left( \frac{\alpha + 2nt}{2t^{1/2}} \right) \right\} \right) \quad (18)$$

where  $n = \sqrt{\beta^2 - k_L a}$ . The equation (18) shows that the collected data in the detector depends on the dispersion of the dissolved gas in the tubes and on the gas-to-liquid dissolution rate in the reactor. The first term of the right hand of the above equation corresponds to the step response for the ozone in water, caused by the dispersion in the flowing system. No information about the mass transfer rate is contained in this term but values as the saturation concentration or the dispersion parameters for the ozone will be necessary to evaluate this function. So, in an independent experiment with water saturated in ozone, the dispersion parameters should be determined previously to use the equation (18). Note that as the transfer process is faster, the coupling between the kinetic and the dispersion process vanishes.

### 3. Transfer function for mass dispersion in continuous flow systems with chemical reaction

As a consequence of the precedent analysis, it is worthwhile to consider now the monitoring of chemical reactions with flow systems. The first required

step to begin this analysis is to reformulate the dispersion problem with a chemical reaction. The conservation equation (1) does not consider the mass apparition or disappearance caused by a chemical reaction, then a source term should be added. Second, the chemical reaction itself should be defined through its kinetics before to state the equations. Let us suppose the easiest case where  $A + B \rightarrow \text{Products}$  and the reaction is of the first order for both reactants. In this case, the governing equations for the dispersion-reaction process can be written as

$$\left. \begin{aligned} \frac{\partial C_A}{\partial t} &= D_A \left( \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} \frac{\partial C_A}{\partial r} + \frac{\partial^2 C_A}{\partial x^2} \right) + u_0 \left( 1 - \frac{r^2}{R^2} \right) \frac{\partial C_A}{\partial x} - k_2 C_A C_B \\ \frac{\partial C_B}{\partial t} &= D_B \left( \frac{\partial^2 C_B}{\partial r^2} + \frac{1}{r} \frac{\partial C_B}{\partial r} + \frac{\partial^2 C_B}{\partial x^2} \right) + u_0 \left( 1 - \frac{r^2}{R^2} \right) \frac{\partial C_B}{\partial x} - k_2 C_A C_B \end{aligned} \right\} \quad (19)$$

where  $k_2$  is the second order rate constant of the chemical reaction. In this case we have a system of coupled partial differential equations that should be simplified to obtain an analytical solution. First, let consider a one-dimensional approach for the dispersion phenomenon. Thus, every equation in system (19) can be written as equation (2) adding the kinetic term. Secondly, suppose that the concentration of A is what we measure with our instrument. Then, we can define two extreme situations: (i) the concentration of B in the tube ( $0 < x < L$ ) is greater than the concentration of A; (ii) the concentration of B vanishes at the entry of the tube.

Let us to suppose the first case where the reactant B is in excess. We can assume the quasi-steady state hypothesis and then,  $C_B = C_{B0} = \text{cnst}$ . Thus, the equation (19) for the measured component in the system, reduces to

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - u \frac{\partial C_A}{\partial x} - k'_1 C_A \quad (20)$$

where  $k'_1$  is the pseudo-first order rate constant of the reaction ( $k'_1 = k_2 C_{B0}$ ). This equation differs with equation (2) in the kinetic term and then, the transfer function (5) cannot be applied to this problem as in the precedent sections.

Applying the Laplace transform method explained above to solve equation (20), the transfer function for a dispersion with a pseudo-first order chemical reaction process is

$$g(p) = \exp \left[ \alpha \beta - \alpha (p + q' \ ^2)^{1/2} \right] \quad (21)$$

where  $\alpha$  and  $\beta$  are the dispersion parameters and  $q' = \sqrt{\beta^2 + k'_1}$ . Once this equation is obtained, the response of the system against every kind of perturbation can be deduced. From a theoretical point of view, the response against a step perturbation is the most interesting one because it can be easily fulfilled in the laboratory. Using eq. (6), the concentration response in the system is

$$C(L, t) = \frac{1}{2} C_0 \exp[\alpha(\beta - q')] \left\{ \operatorname{Erfc} \left( \frac{\alpha - 2q't}{2t^{1/2}} \right) + \exp(2\alpha q') \operatorname{Erfc} \left( \frac{\alpha + 2q't}{2t^{1/2}} \right) \right\} \quad (22)$$

The response of the system is very similar to the pure step concentration, equation (10) although it includes an exponential term. This term accounts for the steady state concentration at the end of the conduction because the term between brackets in equation (22) approaches to one as  $t$  increases. The dispersion process is modified by the fluid flow rate in the conduction. If the steady state value of the concentration is obtained experimentally for different flow rates, a non-linear regression fit can be used to obtain the kinetic rate constant of the chemical reaction.

Lets now suppose the second case where the concentration of reactant B is totally consumed at the beginning of the conduction. In this case the rate constant  $k'_1$  approaches zero and the reaction–dispersion equation (20) can again be reduced to equation (2). Then, the dispersion transfer function (5) can be applied in this situation simply considering the time dependence of the concentration of A inside the reactor but not in the tube. Assuming the situation depicted on figure 1 where the perturbation  $S(t)$  is  $C_A(t)$  and supposing that:

$$C_A(t) = C_0 \exp(-k_1 t) \quad (23)$$

the convolution theorem allows to calculate the expected response  $R(t)$  read in the detector as:

$$C(L, t) = \frac{1}{2} C_0 \exp[\alpha(\beta - q) - k_1 t] \left\{ \operatorname{Erfc} \left( \frac{\alpha - 2qt}{2t^{1/2}} \right) + \exp(2\alpha q) \operatorname{Erfc} \left( \frac{\alpha + 2qt}{2t^{1/2}} \right) \right\} \quad (24)$$

where  $q = \sqrt{\beta^2 - k_1}$ . Note that in this case there is not a steady state concentration because as  $t$  increases, the concentration approaches zero asymptotically. Then, a log-plot of the concentration vs. time leads to a line which slope is equal to the chemical rate constant  $k_1$ .

Equation (22) stands for the time-evolution of the A reactant along the dispersion tube. Then, if the pipe is envisaged as a chemical reactor, this equation describes the behaviour of a plug flow reactor when dispersion is present. This situation is not the most advisable for reactor monitoring because concentrations in the reactor change simultaneously with the concentration towards the detector. Thus, both equations (22) and (24) should be combined when a chemical reaction takes place in the reactor and in the dispersion tube:

$$C(L, t) = \frac{1}{2} C_0 \exp[\alpha(\beta - q'') - k_1 t] \times \left\{ \operatorname{Erfc} \left( \frac{\alpha - 2q''t}{2t^{1/2}} \right) + \exp(2\alpha q'') \operatorname{Erfc} \left( \frac{\alpha + 2q''t}{2t^{1/2}} \right) \right\} \quad (25)$$

where in this case  $q'' = \sqrt{\beta^2 + k'_1 - k_1}$ . Obviously this last equation is more complex to treat than equations (22) or (24) since in this equation the kinetic constants are coupled with each other and then a loss of accuracy in its determination should be expected. The rate constants  $k_1$  and  $k'_1$  have been considered different intentionally because the conditions in the reactor and in the flowing tube can differ. If both constants are equal, equation (25) can be simplified and the kinetic constant  $k_1$  is easily obtained.

Summarising, the formulation of the reaction-dispersion problem implies the solution of the system of coupled partial differential equation (19). A simplified dispersion transfer function (equation (21)) can be deduced when steady state kinetic hypothesis is applied. In some experimental circumstances equation (21) can be reduced to (2) and then the kinetic rate constant determined through equation (24). It is important to keep in mind that the deduction of equation (21) implies a number of severe simplifications and the experimental set up should always account for them.

#### 4. Experimental

In order to validate the dispersion model developed in the precedent section, basic dispersion experiments were carried out using the experimental set-up depicted in figure 1. Two water soluble dyes (Tartrazine and Orange II) were used to confirm the validity of equations (10) and (13) for solute step and pulse perturbation, respectively. The consistency between the calculated dispersion parameters and the experimental operation conditions has also been checked with this data set. Equations (22) and (24) related with dispersion coupled with chemical reaction were analysed considering the fading of phenolphthalein in alkaline media.

A system based on a peristaltic pump commonly used in FIA experiments (Gilson Miniplus 3) was set up for the continuous flow measurements. Teflon tubes which length ranges from 0.75 to 3.0 m and 0.8 mm of inner diameter was used to connect the reactor with the detector. The generation of the steps and pulses was done with a three way injection valve (Rheodyne model 5020) allowing the switching between distilled water and the solution under study. The sample and reactive flows towards a Suprasil® quartz flow cell placed in UV-Vis spectrophotometer (Unicam Helios  $\gamma$ ). Two flow cells (Hellma Mod. 178.710-QS and 178.712-QS) with 10 mm optical path length and a volumes of 80 and 15  $\mu$ l, respectively were used. The data were collected and the equipment controlled with a software developed in our laboratory based on Labview® software. The dispersion parameters  $\alpha$  and  $\beta$  and their confidence intervals were calculated using the non-linear regression routines defined in the software Mathematica® based on the Levenberg-Marquardt algorithm.

For experiments consisting on the injection of concentration pulses and steps in the carrier, a solution of  $4.86 \times 10^{-5}$  M of Tartrazine (Acid Yellow 23, CI

19140, CAS 1934-21-0) provided by Color-Center S.A. was used. This substance shows an absorbance maximum at 427.0 nm and the linearity between the absorbance at this wave length and the dye concentration is guaranteed when the absorbance is below 1.0. The second used dye was the Orange II sodium salt (Acid Orange 7, CI 15510, CAS 633-96-5) provided by Sigma–Aldrich (ref. O-4505). The absorbance of this substance was measured at 438.0 nm. Working solutions consisted in  $10^{-5}$  M solutions adjusted at pH = 5 with HCl.

The chemical reaction considered for the analysis of equations developed in section 3 is the decolouration of the phenolphthalein (Merck PA, ref. 107233, CAS 77-09-8) in alkaline media. This reaction can be considered irreversible when temperature is below 35°C and additionally, in high enough alkaline media, the kinetics can be considered as an example of pseudo-first order reaction [32, 33]. All other chemicals used in this work were of analytical degree. Millipore Elix 3 deionised water was used to prepare all solutions in the experiments.

## 5. Results

The response of the continuous flow system against a Tartrazine step for different flow velocities is shown in figure 2. As the flow rate increases, the inflexion point of the curve moves to the left of the plot increasing its slope. That means that the dispersion process decreases with the increase of the fluid velocity, or conversely, as the flow velocity decreases, the importance of the molecular diffusion of the dissolved substance increases, and then, the dispersion of the solute along the tube. The results shown in figure 2 have been obtained with a tube of 3.0 m long at room temperature, measuring the absorbance at 427 nm using a quartz flowing cell with a volume of 80  $\mu$ l. Parameters  $\alpha$  and  $\beta$  calculated using equation (10) with their error interval calculated for a confidence level of 95% are shown in figure 3a and b, respectively. Open symbols concern data showed in figure 2 with flowing cells of 15 and 80  $\mu$ l, and filled ones have been obtained with similar experiments with a tube length of 2.43 m and a 80  $\mu$ l flowing cell.

The analysis of figure 3a and b leads to some conclusions. First, the volume of the flow-cell has no effect on the observed data because the calculated  $\alpha$  and  $\beta$  parameters are statistically equivalent in the sense that the confidence intervals overlap each other when different flow-cell have been used. This assertion has also been confirmed calculating out the dispersion parameters and the flow-cell residence time,  $\tau_v$ , using equation (16) and the same data set. In this case the quality of the fit was not improved, but the obtained hydraulic residence time was very different to that theoretically expected. That means that the last calculated parameters have not physical meaning in the sense that they do not vary as it is expected from its definition and should be considered as the numerical output of the minimisation routine. This is the result of using non-linear regression

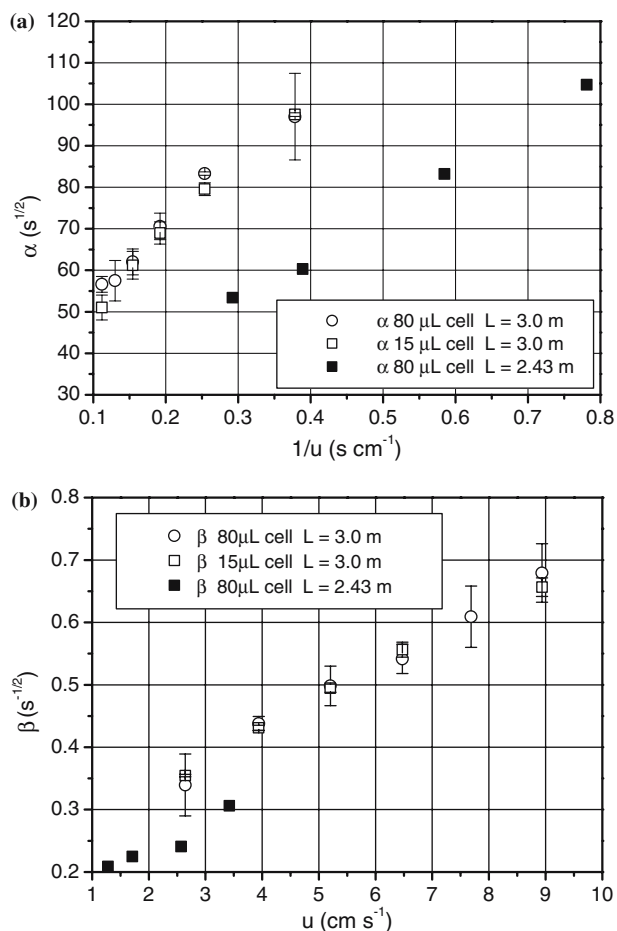


Figure 3. Dispersion  $\alpha$  (a) and  $\beta$  (b) parameters calculated from steps experiments collected in figure 2. The open symbols were calculated from a flowing system length of 3.0 m and the filled ones from other of 2.43 m. The volume of the flow-cell is indicated in the legend.

techniques, which do not ensure the correctness of the calculated values parameters just with the convergence of the model with the experimental data.

Second, from the initial definition of  $\alpha$  and  $\beta$ , these parameters should be independent and directly proportional to the flow velocity,  $u$ , respectively. From experiments it can be observed (see figure 3a and b) that as  $u$  increases,  $\alpha$  decreases and  $\beta$  increases linearly. Furthermore, from these definitions and depending on the plot used for calculations, the dispersion coefficient,  $D_a$ , ranges from 20 to 100 cm<sup>2</sup> s<sup>-1</sup>. This value is several orders of magnitude higher than the usual values for dissolved molecules in water, so other phenomena should explain this estimation. Aris–Taylor model is a convenient approach to the problem of the dispersion of a solute in a flowing fluid. In this model, the

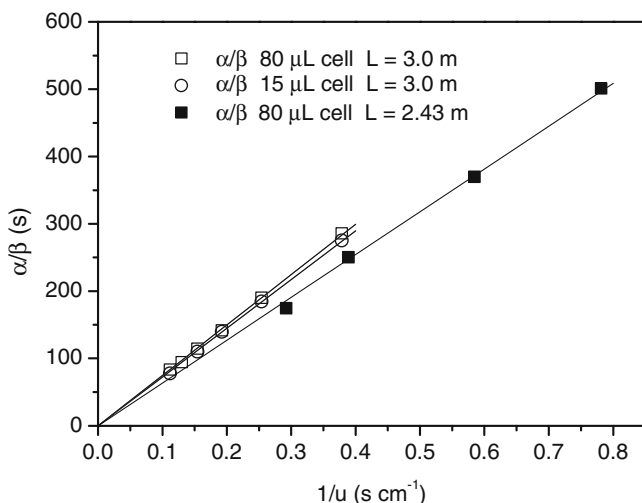


Figure 4. Dependence of the dispersion parameters ratio against the inverse of the flow velocity. The slope of the lines allows the calculation of the effective length of the dispersion system.  $T = 293 \text{ K}$ ,  $[\text{Tartrazine}] = 4.86 \times 10^{-5} \text{ M}$ ,  $\lambda = 427 \text{ nm}$ .

contribution of the radial dispersion to overall process is averaged over the tube section leading to equations (2) and (3) [6, 8, 24]. Thus, the definition of the  $\alpha$  and  $\beta$  parameters considering Aris–Taylor model should be rewritten as

$$\alpha_T = \frac{L\sqrt{48D_m}}{uR}, \quad \beta_T = \frac{\sqrt{48D_m}}{2R} \quad (26)$$

According to these equations,  $\alpha_T$  is inversely proportional to the mean flow velocity as the experiments confirm, but the dependence between  $\beta_T$  and  $u$  remains unclear. A dependence between these parameters can be explained considering that the dispersion parameter  $\beta_T$  comes from the simplification of a more general differential equation. Any simplification in a differential equation results in a loss of information in the deduced parameters. Then, unexpected dependencies with experimental conditions as those detected here, can be observed due to the incompleteness of the mathematical model.

Another appropriate representation to obtain relevant information of the dispersion system is to plot the ratio  $\alpha_T/\beta_T$  against the inverse of flow velocity (see figure 4). From equation (26) this quantity should be proportional to the dispersion length,  $L$ , and inversely proportional to the flow velocity. The calculated lines from the data agree with this prediction but their slopes are greater than the expected value. Considering that this value should be interpreted as an equivalent length which considers all the pipe fittings along the tube, this figure should be used in the calculation of the diffusion coefficient of the solute.



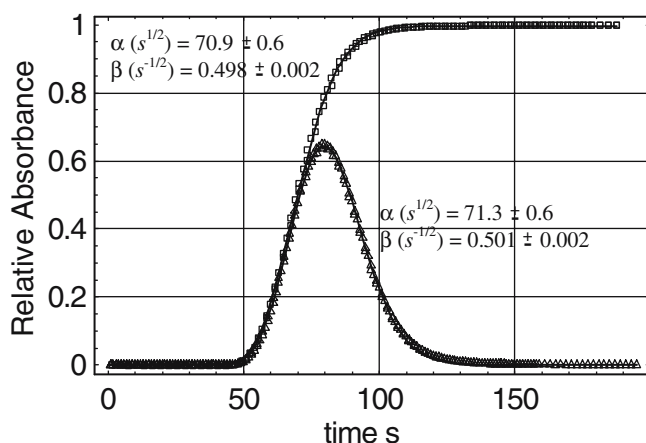


Figure 5. Comparison between the step and pulse experiments of Tartrazine dye solutions. The flow velocity for both experiments is  $5.20 \text{ cm s}^{-1}$ , the dispersion length of  $3.0 \text{ m}$  and the flow-cell volume of  $80 \mu\text{l}$ . The pulse duration was set to  $20 \text{ s}$ . The dispersion parameters were calculated for the step and the pulse using equations (10) and (23) respectively. The curves are the best fit of the data to those equations.  $T = 293 \text{ K}$ ,  $[\text{Tartrazine}] = 4.86 \times 10^{-5} \text{ M}$ ,  $\lambda = 427 \text{ nm}$ .

Combining the results shown on Figures 3a and 4, the value of the diffusion coefficient of the Tartrazine ranges from  $8.78 \times 10^{-6}$  to  $3.80 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

So far, equation (10) together with Aris–Taylor model has been proved as a good description of the experimental data set. Now the validity of calculated parameters should be proved with independence of the experimental set-up, that is, with independence of the selection of one kind of experiments among others. All the above dispersion parameters and the magnitudes derived from them have been obtained with steps experiments, so we need know if these parameters are correct with independence of the experiment carried out. The simplest way to prove this is to perform other kind of experiments and to compare the parameters calculated out. With this aim, pulse experiments were designed to compare the calculated parameters in equations (13) and (10) (see section 2.1). In this case, the input concentration in the dispersion tube was applied during a known period of time,  $\tau$ . In figure 5 the response of the flowing system for a pulse of  $20 \text{ s}$  is shown. The lines are the best fit curves from experimental data. The data of three independent series for the step and the pulse are plotted. The dispersion parameters calculated out for each experiment are next to the curves. The agreement between both calculations is remarkable and confirm the validity of the mathematical equations presented in this paper for the dispersion of a solute in a flowing system.

Let us consider with more detail the effect of the tube length on dispersion. A new series of experiments with Orange II were carried out. We were

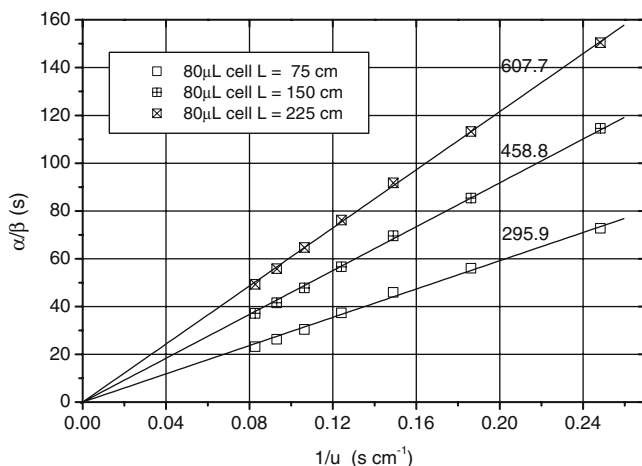


Figure 6. Effect of the length of the dispersion tube on the  $\alpha/\beta$  ratio. The experiments were carried out with Orange II measuring the solution absorbance at 438 nm. The legend shows the length of the section between the injection valve and the detector (see figure 1) The slope of the lines gives the effective length,  $L_{eq}$ , of the system.  $T = 293$  K, [Orange II] =  $10^{-5}$  M, pH = 5.

interested in the determination of the diffusion coefficient of this substance in water simultaneously with the influence of the tube length on dispersion parameters. The tube section of our experimental set-up placed between the injection valve and the detector can be easily changed. Segments of 75, 150 and 225 cm were intercalated maintaining the other experimental conditions. Figure 6 shows the effect of the different sections in the response for a Orange II step. Let's consider now that the length in the Aris–Taylor model (see equation (26)) is an equivalent length,  $L_{eq}$ , which is the sum of the replaceable section,  $L$ , plus a constant  $\lambda$  which accounts with the pipe fittings, pump tubes, valves and all possible additional sections not considered in the overall distance between the sampling port and the spectrophotometer cell. This distance  $\lambda$  does not change between successive experiments. Then,  $L_{eq} = L + \lambda$ . As in the case of the Tartrazine, the ratio between the two dispersion parameters gives us twice the equivalent length,  $L_{eq}$  (see figure 6). Plotting the slope of each line of Figure 6 against the length of the interchangeable section,  $L$ , a line with slope 2 should be obtained. Figure 7 shows this result. The slope is close to the expected value and an additional length of the system,  $\lambda = 71$  cm, should be considered in further calculations. Using these values, it is deduced that the diffusion coefficient of the Orange II ranged between  $8.5 \times 10^{-6}$  and  $2.1 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>.

Until now, the dispersion of a solute without chemical reaction has been considered. In Section 3 a transfer function for a dispersive reacting solute has been derived assuming a first order kinetics. In order to check the derived equations, the reaction of fading of phenolphthalein in alkaline media has been studied. It is known that this substance when it is used as indicator in an acid-base

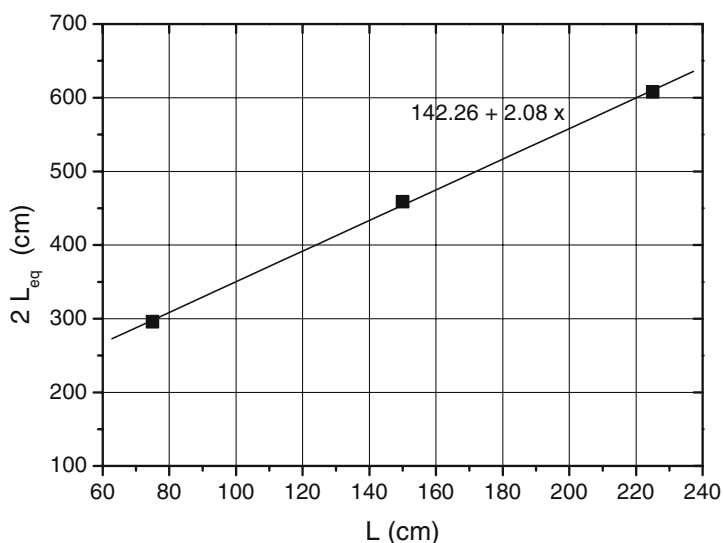


Figure 7. Consistency test of the calculated effective length in figure 6 (see details in the text). The expected slope of the line is 2. The interception gives twice the additional length of the tube,  $\lambda$ .

titration, the intensity of the colour at the end point evanesces or disappears after some period of time. At low temperatures and high pH, this reaction could be considered as an irreversible pseudo-first order reaction [32, 33].

Previously to the study of the chemical reaction, the characterisation of the dispersion of the phenolphthalein in water is necessary. Because this characterisation cannot be carried out when this substance is in its coloured form because of the chemical reaction, the concentration of the phenolphthalein was followed measuring its ultraviolet absorption band at 275 nm. The dispersion curves are showed on figure 8. The same dependence between the parameters and the fluid velocity has been previously observed with the water soluble dyes. The calculated diffusion coefficient of the phenolphthalein at 298 K with this series of experiments was  $7.59 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

Figure 9 shows the evolution of the absorbance of the phenolphthalein reacting in alkaline media measured at 550 nm. The curves were recorded at different fluid velocity. The arrow indicates the increasing velocity. In these experiments,  $[\text{OH}^-]_0 = 0.2 \text{ M}$  and  $T = 298 \text{ K}$ . The lines shows the best fit of data to equation (25) considering that the kinetics inside the reactor, characterised by the constant  $k_1$ , does not differ from the reaction rate along the dispersion tube, characterised by  $k'_1$ . As the velocity of the fluid increases, the maximum of the curve increases because the lower the residence time in the tube. For long times, all curves coalesces to the same one as is expected by the exponential term in equation (25).

Modifying the initial pH conditions the rate constant is modified as is expected for a pseudo-first order reaction. In figure 10 the effect of the  $\text{OH}^-$

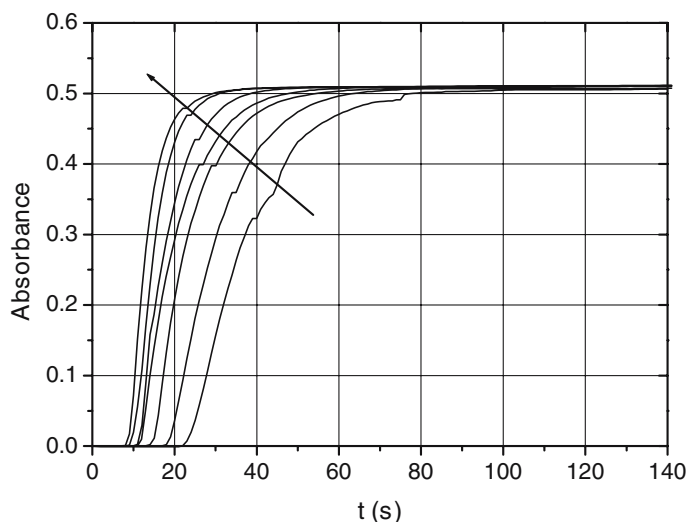


Figure 8. Dispersion curves of phenolphthalein in aqueous solution measuring the absorbance at 275 nm.  $[\text{Phenolphthalein}] = 1.25 \times 10^{-4} \text{ M}$ ,  $L = 150 \text{ cm}$ ,  $T = 299 \text{ K}$ . The arrow indicates the increasing flow velocity.

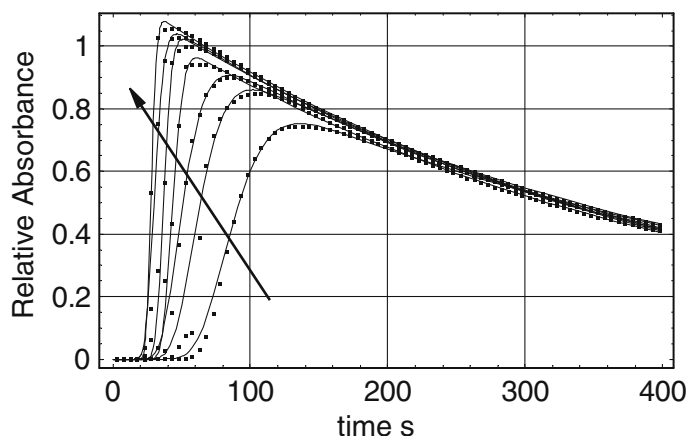


Figure 9. Dispersion curves of reacting phenolphthalein in alkaline media at  $\text{pH} = 13.3$ . The absorbance was measured at 550 nm.  $[\text{Phenolphthalein}]_0 = 1.25 \times 10^{-4} \text{ M}$ ,  $L = 314 \text{ cm}$ ,  $T = 298 \text{ K}$ . The arrow indicates the increasing flow velocity. The curves are the best fit of data to equation (25) with  $k'_1 = k_1$ .

concentration is shown. Increasing the pH the reaction evolves faster. Plotting the calculated reaction rate against the hydroxyl concentration a straight line is obtained (see figure 11). The slope gives the second order rate constant of the reaction equal to  $1.33 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 298 K which agrees with the value previously reported by Massod et al. [33]

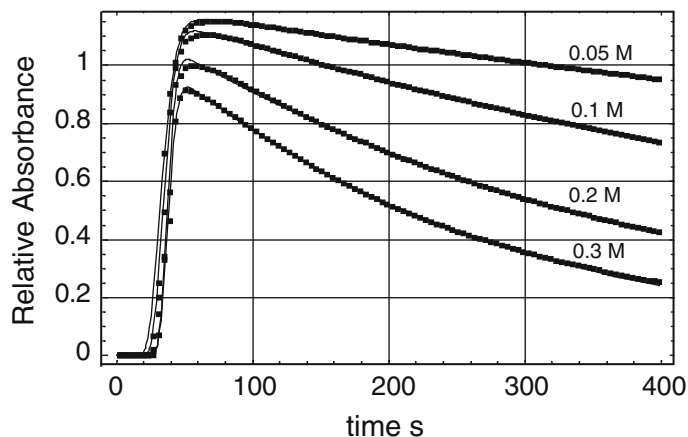


Figure 10. Effect of the  $[\text{OH}^-]_0$  on the dispersion curves. The phenolphthalein fading follows a pseudo-first order kinetics. Increasing the pH the reaction is faster. The flow velocity in these experiments was  $9.65 \text{ cm s}^{-1}$ .  $[\text{Phenolphthalein}]_0 = 1.25 \times 10^{-4} \text{ M}$ ,  $L = 314 \text{ cm}$ ,  $T = 298 \text{ K}$ . The curves are the best fit of data to equation (25) with  $k'_1 = k_1$ .

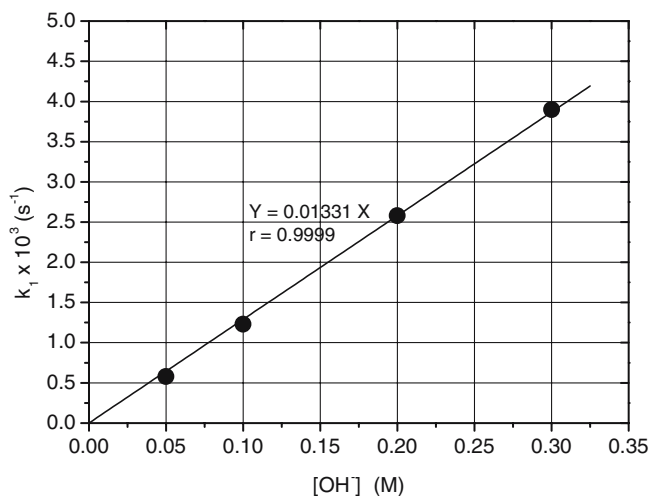


Figure 11. Determination of the second order reaction rate constant for the phenolphthalein fading in alkaline media. The pseudo-first order rate constants were evaluated from the dispersion curves of figure 10. The slope gives a rate constant of  $0.0133 \text{ M}^{-1} \text{ s}^{-1}$  at  $298 \text{ K}$ .

## 6. Conclusion

The transfer function formalism for continuous flow analysis systems presented in this work gives an appropriate theoretical framework to explain some simple experimental situations for continuous monitoring of chemical reactors. The advantage of this approach is that allows to combine sequentially the

transfer function of different phenomena and by Laplace inversion, to obtain the response of the system. The computational limitations of the method is related with the difficulties of the Laplace inversion. This limitation can be overcome always using repeatedly the convolution theorem which at each level of recursion it will increase the complexity of the obtained solution.

This approach also allows to define semiempirical parameters which are related with geometrical or physicochemical properties of the system under study, i.e. tube length and radius, flow velocity, diffusion coefficient, etc. In this work the definition of two dispersion parameters in combination with the Aris–Taylor dispersivity coefficient gives a reasonable explanation of the experimental observations when no chemical reaction occurs. But experiments also reveals some unattended results. The most significant is the linear dependence of  $\beta$  with the flow velocity. The discrepancy between the Aris–Taylor model and the experimental observations should be explained as a consequence of the simplifications steps done to reduce the equation (1) to its one-dimensional form (2). Any simplification of a differential equation leads to a lost of some information about the original equation. References considering theoretical aspects of dispersion are prolific, but a lesser number of references focused on the connection between the macrotransport theory with experiments can be found (see ref. 24 and references herein). The transfer function for dispersion processes obtained in this work has been derived from the macrotransport one-dimensional equation allowing then, to check few aspects of the theory. The theory does not predict how the experimental behaviour of the parameter  $\beta$  is, and that also has a consequence for the parameter  $\alpha$ . In fact, after the non-linear fitting if the autocorrelation matrix is analysed, a strong correlation between both experimental parameters is observed. This correlation is also confirmed by figure 4 where the ratio between  $\alpha$  and  $\beta$  is proportional to the inverse of the flow velocity. Thus, this discrepancy between the experimental observations and the theoretical model could be the consequence of some presumption in the model which is not appropriate for the physical system or some other physical phenomena should be considered in junction with the solute dispersion, i.e. the effect of pulsating flows by the peristaltic pumps.

When reacting systems are considered, the same dependence and correlations between the parameters are observed. Although the approximation to this problem in this work has been done by the analogy with the differential equation in non-reacting systems, the derived equations show a good agreement when simple kinetics apply. The advantage of the transfer function formalism respect other distributed models based on the residence-time distribution functions [1, 13, 14] is that there is a direct correspondence between the statistical properties of the curve and the calculated dispersion parameters. Moreover, this approach allows to consider more complex processes such as the presence of mixing chambers along the dispersion line, chemical reactions outside and inside the dispersion tube, etc. However, the combination of transfer functions in these

circumstances should be considered carefully because unexpected correlations can appear between previously unconnected parameters. A further analysis of the parameters will prove if the calculated constants are just the result of a non-linear fitting or if they are consistent with some experimental and physical constraints.

Finally an additional commentary about other potential uses of the transfer function formalism applied to continuous analysis systems. The advantage of a transfer function in a dynamical system is that, at least theoretically, the information of an arbitrary perturbation can be recovered from the analysis of the measured response. In this work the convolution of the transfer function (5) has been exploited, but the deconvolution of response of continuous analysis systems should be also considered as an application of transfer function formalism. Furthermore, in this situation the derivation of a transfer function with an exact physical meaning is not a prerequisite for deconvolving (or unfolding) the signal. It is sufficient to have a good enough empirical transfer function describing the system behaviour to proceed to the deconvolution. Thus, the transfer function formalism presented in this work should be considered as a tool which can be used to predict the measured response of the system if the applied perturbation it is previously known, or to reconstruct the original perturbation from the measured response and the transfer function of the system.

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