

# Theoretical Considerations of Flow Injection Analysis in the Absence of Chemical Reactions

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## Abstract

The fundamental mechanism of Flow injection analysis (FIA) is assumed to be simple diffusion and the response of the detector is included in a model description that provide information about the shape of the FIA peak in terms of, basically, five parameters. Two of the five parameters are associated with the compound while the rest yield information about the solvent and friction. By introducing a kinetic-diffusion coefficient, it is shown that the shape of the FIA peak is well described by the theory for diffusion of  $K_3[Fe(CN)_6]$ ,  $K_2CrO_4$  and  $Ni(NO_3)_2$  in distilled water. It is suggested that any deviation from the features of the present model and the results of a tentative chemical reaction with one of the test compounds, is related to chemical kinetics.

**Keywords** Diffusion, theory, spectrophotometry, segment flow, friction

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## 1. Introduction

This year, celebrating its 25th year of existence, FIA [1] has proven to be a versatile and simple method of chemical analysis and more than 10.000 articles have now been published worldwide [2], which evidence the great impact of the technique on analytical chemistry. Since the invention of FIA, the great majority of theoretical descriptions have rested on the Poiseuille model [3-6] and the diffusion-convection equation [3, 7-8]. In these formulations, the calculation of the precise flow profile of the FIA peak itself, requires considerable computational efforts and imposes time consuming steps in the full application of theoretical comprehension's of the results. Thus, in most FIA investigations, physical and chemical characteristics of the system are not implemented in the interpretation of results. Therefore, there is a great need for a tool that, to a higher degree, enables concatenation of theory and experiments. In order to meet this demand, it is worthwhile to introduce a few assumptions that simplifies the theory but, on the other hand, do not compromise the general chemical and physical insight into the system. In the present work, such a description was developed and it is based on the assumption that the single important mechanism that

governs the time evolution of the injected segment is diffusion. Any other feature related to the dynamics of flow, is proposed to provide minor contributions to the FIA signal obtained. By using these assumptions, a simple model was developed and validated on three test compounds. The validation provided a limited number of parameters that allowed separation of diffusion characteristics of the test compounds from internal friction of the tubular system.

## 2. Experimental

In order not to confuse diffusion with turbulent mixing phenomena within the tubes of a FIA manifold, an experimental setup was designed with a  $5 \cdot 10^{-4}$  m bore and with straight tubes throughout (Fig. 1). In this manner, the injected solute segment experience no obstructions in the form of indentations or tanks of dilution. Thus, the flow is considered to be strictly of laminar type and with a small Reynolds number [9]. A peristaltic pump was used to maintain a constant flow rate and the detector was a HP8452A UV-VIS photometer with photodiode detection (350 nm). The width of the detection cell was 0.01 m. The solutions were prepared with the following concentrations:  $[K_3(Fe(CN)_6)] = 5 \cdot 10^{-3} M$ ,

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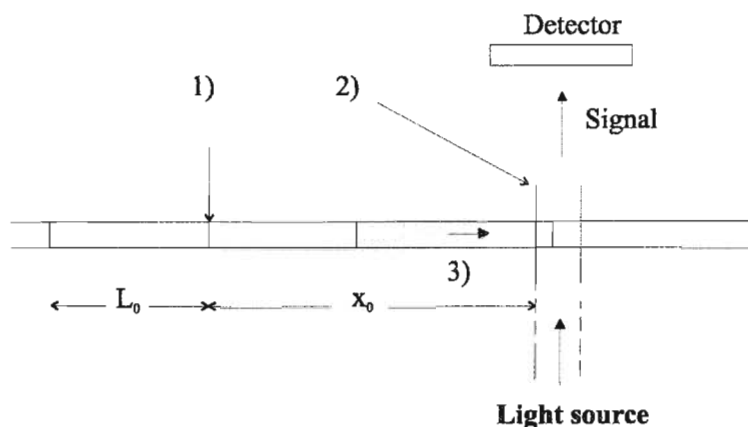


Fig. 1 Experimental setup for the FIA measurements. In the simplest possible arrangement, the segment (1) of initial length  $L_0$  was injected into the carrier and after traversing the distance  $x_0$  the absorbance was registered at the detection cell (2). Subsequent to injection, the length of the segment (3) expands exponentially with time owing to diffusion.

$[K_2CrO_4] = 4 \cdot 10^{-3} M$  and  $[Ni(NO_3)_2] = 10^{-1} M$  and they were chosen as to ensure that the signals obtained displayed absorbances that were significantly above the noise level for all varieties of flow rates and tube lengths. Furthermore, all absorbances measured fall within the linear range of response, that is, the measured peak height never exceed the maximum absorbance of linear response. The chemicals used for preparation of test solutions were of analytical grade (Merck p.a.) and diluted with distilled water.

### 3. Theory

If the flow in FIA were considered to be of simple type, that is, plug-like [10] or segmental [11], the three mechanisms that govern molecular movements are translation, by the action of the pump, diffusion and friction. First order diffusion may be described in terms of an exponential function that accounts for the variation in concentration,  $c(t)$ , as a function of time ( $t$ ). This result was obtained by solving Fick's first law of diffusion by assuming a constant concentration gradient, that is,  $D \cdot dc/dx = D_x \cdot c(t)$ . When the initial concentration in the segment before injection is denoted as  $c_0$ , the absorbance (Beer-Lambert) after injection becomes:

$$A(t) = \varepsilon \cdot l \cdot c(t) = \varepsilon \cdot l \cdot c_0 \cdot \exp(D_x \cdot t) = A_0 \cdot \exp(D_x \cdot t) \quad (1)$$

where  $D_x$  is the diffusion component along the tube axis,  $\varepsilon$  is the molar absorptivity and  $l$  is the width of the detection cell. In the following, the initial concentration and the diffusion component may be functions of both distance and flow rate. According to eq. 1, the length,  $L(t)$ , of the injected segment, of initial length  $L_0$ , expands exponentially as a function of time:

$$L(t) = L_0 \cdot \exp(-D_x \cdot t) \quad (2)$$

Since the expansion proceeds while the segment is measured in the detection cell (Fig. 1), the signal increases momentarily, as followed by the absorbance, but decreases simultaneously owing to dilution by the solvent. Such events where the absorbance increases under the influence of a decreasing signal may be conveniently described by  $(1 - \exp(D_x \cdot t))$  [1, 12] and the simultaneous decrease in signal follows eq. 1. Thus, a delta function signal,  $\delta(t)$ , that reaches the detector yields a response given by convolution (\*) of

the delta function with the signal increase/decrease function [13]:

$$R(t) = \delta(t) * (1 - \exp(D_x \cdot t)) \cdot \exp(D_x \cdot t) \\ = (1 - \exp(D_x \cdot t)) \cdot \exp(D_x \cdot t) \quad (3)$$

However, if the initial signal was a constant, say  $A_0$ , the obtained signal were found by the convolution of  $A_0$  with eq. 3 [13]:

$$A_R(t) = \begin{cases} \int_{t_0}^t A_0 \cdot R(t-\tau) d\tau & t_0 \leq t \leq t_1 \\ \int_{t_1}^t A_0 \cdot R(t-\tau) d\tau & t \geq t_1 \end{cases} \quad (4)$$

which yields the two functions that describe the FIA peak itself:

$$A_1(t_0 \leq t \leq t_1) = -A \cdot [\exp(D_x \cdot (t-t_0)) - 1]^2 \\ A_2(t \geq t_1) = A \cdot \exp(D_x \cdot t) \\ \bullet (\exp(-D_x \cdot t_0) - \exp(-D_x \cdot t_1)) \\ \bullet [2 - \exp(D_x \cdot t) \cdot (\exp(-D_x \cdot t_0) + \exp(-D_x \cdot t_1))] \quad (5)$$

where the constant  $A$  may depend on distance and flow rate, since  $A = A_0 / (2 \cdot D_x)$ . Equation 5 predicts that the tail of the FIA peak decreases exponentially as a function of time in accord with previous results [1, 12]. The time values  $t_0$  and  $t_1$  should be determined by adding the  $x$ -component of the diffusion velocity ( $v_d$ ) to the linear flow rate ( $v_x$ ) [11]. Upon integration of the equation of motion, the time of arrival  $t_0$  may be found from the transcendent equation [11]:

$$x_0 = \frac{1}{2} \cdot L_0 \cdot [\exp(-D_x \cdot t_0) - 1] + v_x \cdot t_0 \quad (6)$$

Where  $x_0$  is the distance from point of injection to the cell of detection. An approximate value of  $t_0$  may be found by expanding eq. 6 to first order:

$$t_0 \cong \frac{2}{2 \cdot v_x - D_x} \cdot x_0 \quad \left| -D_x \cdot t_0 \right| \leq 1 \quad (7)$$

The time  $t_1$  has been found to be equal to the time of arrival to the detector of the mid-section of the segment, which also coincide with the time of peak maximum [11]:

$$t_1 = t_M = \frac{x_0 + L_0 / 2}{v_x} \quad (8)$$

Thus, the linear flow rate can be found from measuring the time of peak maximum (eq.8) and the diffusion parameter can be estimated by the time of onset ( $t_0$ ), as given by eq. 7. In this manner, two independent values of  $D_x$  may be obtained by fitting eq. 5 and eq. 7 to experiments and they should, of course, correspond. The area,  $\Lambda$ , of the FIA peak is found by integration of eq. 5 and it reduces to the simple expression:

$$\Lambda = -\frac{A_0}{2 \cdot D_x} (t_1 - t_0) \quad (9)$$

which shows that knowledge of the time of onset ( $t_0$ ) and the time of exit ( $t_1$ ) are essential and that they should be modified by a factor containing information about initial absorbance and diffusion.

#### 4. Results and discussion

Three different compounds were tested and it was found by fitting eq. 5 to experiments that the constant  $A_0$  (eq. 4) depends on distance and flow rate in the following manner:

$$A_0 = k_0 \cdot \exp(k_1 \cdot x_0) + k_2 \cdot v_x \quad (10)$$

and similarly, the diffusion constant of eq. 1 also becomes a function of distance and flow rate:

$$D_x = k_3 \cdot v_x + k_4 \cdot x_0 + k_5 \quad (11)$$

where a set of six constants ( $k_0, \dots, k_5$ ) characterise the given system as shown in Table 1. An example of fitting eq. 5 to the experimental data is portrayed in Fig. 2, where eight FIA peaks are depicted as a function of distance for  $K_3 [Fe(CN)_6]$ . There is a very good correspondence between theory and experiment and this particular result allows

Table 1 Friction parameters and diffusion parameters of eqs. 9 and 10, as obtained by fitting eq.5 to experiments.

Constants Compound	$k_0$ (abs.)	$k_1$ ( $m^{-1}$ )	$k_2$ (abs.·s· $m^{-1}$ )	$k_3$ ( $m^{-1}$ )	$k_4$ ( $m^{-1}$ · $s^{-1}$ )	$k_5$ ( $s^{-1}$ )
$K_3[Fe(CN)_6]$	2.1	-1.5	13.5	-3.0	0.09	-0.26
$K_2CrO_4$	1.1	-1.3	14.8	-6.1	0.1	-0.33
$Ni(NO_3)_2$	1.7	-1.0	13.3	-8.6	~ 0	-0.32

determination of  $k_0$ ,  $k_1$ ,  $k_4$  and  $k_5$  (Table 1). The minor deviations between experiment and theory at the tail part of each individual peak, is proposed to be due to a concentration profile that is trapezoidal shaped rather than rectangular in shape as anticipated by the present theory. The constant  $k_0$  is related to the magnitude of the initial absorbance, that is, the absorbance of the segment measured before injection, which corresponds to the absorbance ( $A_0$ ) measured if the test solution were constantly fed to the detection cell. In all three cases, the value of  $k_0$  exceeded the value of corresponding absorbances,  $A_0$ , which were determined as 1.3, 0.84 and 0.73 for  $K_3[Fe(CN)_6]$ ,  $K_2CrO_4$  and  $Ni(NO_3)_2$ , respectively.

Tentatively, it is suggested that the  $k_0$ -values of Table 1, are absorbances of the compounds themselves, i.e., the solvent-free absorbances. The constants  $k_1$  and  $k_2$  do not differ very much among the three compounds (Table 1). Neither does the constant  $k_4$  that is relatively small, which shows that the dependence of  $D_x$  on distance ( $x_0$ ) is weak, as compared to the other constants of eq. 10. If the absorbance profile of the segment were considered to be trapezoidal rather than rectangular [10] it has been shown earlier [11] that the dependence of  $D_x$  on  $x_0$  is indifferent from zero, which further simplifies eq. 10 ( $k_4 \cong 0$ ). The rectangular absorbance profile of the present work (eq. 4) may be considered to be an

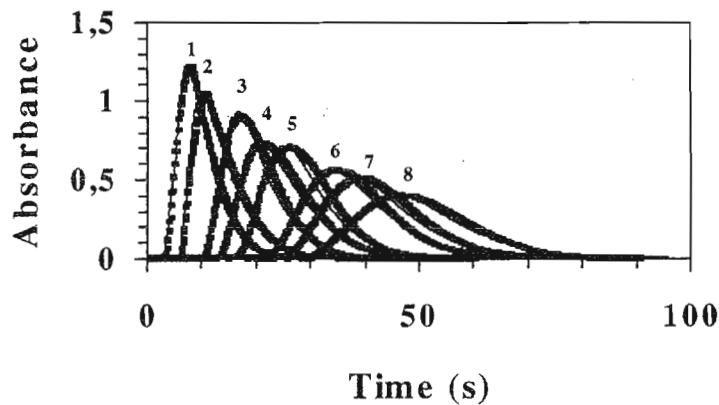


Fig. 2 Experimental FIA peaks of  $K_3[Fe(CN)_6]$  (horizontal bars) and theory (solid line) according to eq. 5, shown for various distances ( $x_0$ ). The FIA peaks of short distances are tall and narrow (to the left) while the peaks of long distances are wide and small (right side).  $x_0 =$  (1): 0.2, (2): 0.4, (3): 0.6, (4): 0.8, (5): 1.0, (6): 1.4, (7): 1.6 and (8): 2.0 m.  $v_x = 0.0424 ms^{-1}$  and  $L_0 = 0.168 m$ .

approximation in relation to a more general description using a trapezoidal shape. Accordingly, the constant  $k_4$  is considered to be approximately independent of the chosen test compound, which is also a valid statement for the constants  $k_1$ ,  $k_2$  and  $k_5$  (Table 1). Thus, the only constants that are of chemical interest, as such, are  $k_0$  and  $k_3$  whereas the other constants are associated with the physical functionality of the FIA system. Within good precision, the physical constants of the present system therefore become:

$$k_1 = -1.3 \pm 0.2 \text{ m}^{-1}, \quad k_2 = 13.9 \pm 0.7 \text{ abs.} \cdot \text{s} \cdot \text{m}^{-1}$$

and  $k_5 = -0.30 \pm 0.03 \text{ s}^{-1}$ . The reciprocal value of  $k_1$  is a characteristic length that, in association with  $k_2$ , reflects the internal friction of the tubular system.

The constant  $k_5$  corresponds to the characteristic response time of the detector, i.e., it has nothing to do with the chemical or physical flow dynamics but is simply a measure of how fast the detector is responding. This value is important to know, since it limits the rate of chemical reactions that can be studied by the apparatus. As noted above the constant  $k_0$  equals the initial absorbance of the segment and is thus accounted for, while  $k_3$  is a new useful constant

that characterises the diffusion behaviour of a given compound.

Now, when all the parameters of eq. 9 are known in terms of distances, constants and flow rates, it is possible to reach an approximate expression for the area of the FIA peak:

$$\Lambda = \frac{k_0 \cdot \exp(k_1 \cdot x_0) + k_2 \cdot v_x}{k_3 \cdot v_x + k_4 \cdot x_0 + k_5} \cdot \left( \frac{x_0 + L_0/2}{v_x} - \frac{2 \cdot x_0}{2 \cdot v_x - (k_3 \cdot v_x + k_4 \cdot x_0 + k_5) \cdot L_0} \right) \quad (12)$$

In Fig. 3, the area is depicted as a function of distance for five different flow rates and it shows that within a wide range of distances, the area is almost constant and, furthermore, that a maximum value of the area exists for a characteristic distance (not simple). The area proportionality to inverse flow rate ( $v_x$ ), as predicted by eq. 12, is in agreement with earlier findings [12]. The main equations (1, 5, 6, 12) of the present description show that without any chemical reactions, the flow may be expressed in terms of diffusion and friction. If the constants  $k_0 \dots k_5$  were known for the compounds of a given chemical reaction, it would be possible to extract information

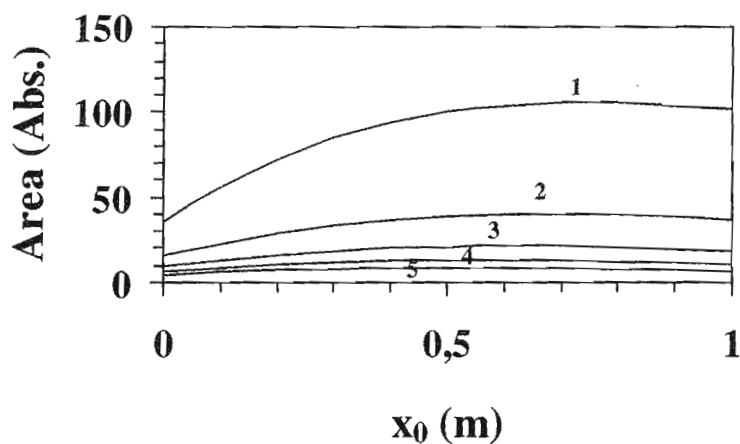


Fig. 3 The approximate area of the FIA peak given by eq. 12. In the calculation, five different linear-flow rates ( $v_x$ ) were used. (1): 0.01, (2): 0.02, (3): 0.03, (4): 0.04 and (5): 0.05  $\text{ms}^{-1}$ .  $x_0 = 1.0 \text{ m}$  and  $L_0 = 0.2$ .

about chemical-reaction kinetics by means of the present equations. The equations describe the flow in two dimensions and deviations from the expected behaviour of solute molecules of reactants according to eq. 5 may be assigned to a potential chemical reaction. Preliminary results indicate that there is no fundamental difference between the shape of FIA peaks obtained by chemical reactions, as compared with the shape of FIA peaks obtained by the present model.

## 5. Conclusions

By assuming simple diffusion of first order, a 2-dimensional model description of the FIA profile was obtained, which enables extraction of information about chemical kinetics in tubular systems. Diffusion is understood by a kinetic-diffusion coefficient ( $k_3$ ) that is measured in units of reciprocal meters. The model applies to systems of pure diffusion as well as to systems involving chemical reactions and it allows separation of diffusion phenomena from friction and from chemical kinetics.

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