Mathematical Modeling of Flow-Injection Techniques and their Applications for Environmental Monitoring

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Abstract

A classification of the existing mathematical models of flow-injection (FI) manifolds based on the main principles on which they are built, have been proposed. Numerous mathematical models of FI systems employing ideas from different scientific areas (e.g. mathematical statistics, chemical engineering, chromatography) have been developed so far. The models have been compared with respect to their predictive power, the complexity of their mathematical treatment, and the requirements for computation time when applied to single-line, multi-channel and conjugated two-line FI systems. It is concluded that the axially dispersed plug flow model deserves special attention because it offers an acceptable compromise between the conflicting requirements for maximal possible mathematical simplicity and maximal possible precision. Applicability of these existing flow-injection models to single-line, multi-channel and conjugated two-line systems for environmental monitoring have been discussed.

Introduction

Flow-injection (FI) first described by Ruzicka and Hansen [1] as an unsegmented flow technique in which a volume of liquid sample (typically 10-200 µL is inserted into a moving liquid carrier stream, where it undergoes physical dispersion as it is transported to a flow-through detector for measurement. The response is in the form of a peak, the height of which is usually directly related to analyte concentration. The degree of sample dispersion is highly reproducible and is controlled by factors such as flow rate, manifold geometry, and tubing length and diameter. Though the principles on which FIA is based are well understood, and extensively implemented in the analytical practice, the development of its theoretical foundations summarized in numerous books [2-3] and reviews [4-5] is far from completed. The main reason for this fact is the complexity of the phenomena (e.g. diffusion, convection, chemical kinetics) taking place in flow-injection (FI) systems and their interrelation. Another obstacle in this respect is the variety of FI configurations (e.g. single- and multi- line systems with one or several confluence points, mixing chambers, dialysis and gas-diffusion modules, open-closed systems, etc.) and modes of operation (e.g., stopped, reversal, and sinusoidal flow). Numerous mathematical models based on various principles borrowed from different scientific areas (e.g., mathematical statistics, chemical engineering, artificial intelligence, chromatography) and thus exhibiting different drawbacks and advantages have been developed. A sound classification incorporating all these models and based on the main principles on which they are built is required for allowing an impartial comparison between them. It will assist a researcher in choosing an appropriate model according to the concrete FI system to be modeled and the tasks which are supposed to be fulfilled by the model.

The present review outlines a classification of the existing mathematical models of FI manifolds and considers their applicability for the description of the main component flow-through elements of three basic FI configurations, i.e., the single-line system, the multi-line system and the conjugated two-line system. The aim of this work

was to (i) develop a mathematical model enabling further optimization of analysis, and (ii) to validate the model on real experimental data. Present interest has also focused on the use of Flow Injection Analysis (FIA) for in situ monitoring of environmental matrices, particularly natural waters.

Category of flow-injection models

According to the way FI manifolds are mathematically modeled, they fall into two main classes known as the so-called "black box" and analytical experimental models (Figure 1). The types of models comprising these two classes will be briefly considered in the subsequent paragraphs.

"Black box" models

These models are frequently applied because of their relative mathematical simplicity which does not necessarily imply fast computations (e.g., neural network training may be extremely time consuming). The main drawbacks of these models are the requirements for a large number of experiments for their development, their applicability only to the conditions and manifold components used for the evaluation of their parameters, and their inability to allow a deeper insight into the physics and chemistry of the processes they describe. The "black box" models can be divided into several subgroups depending on the specific approach they utilize
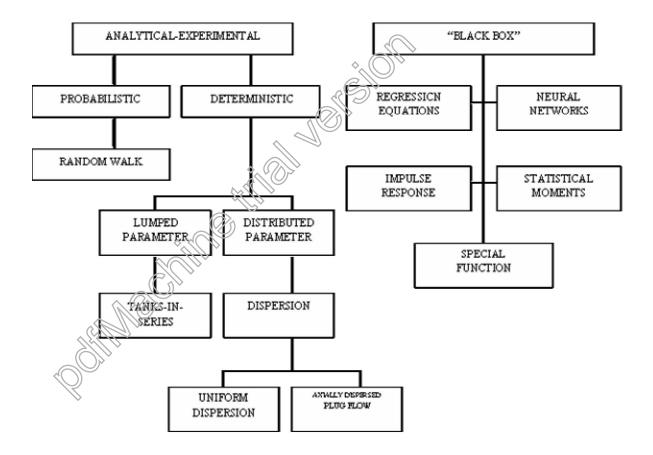

Fig. 1. Mathematical models of Flow-Injection systems

Regression equations

The most frequently encountered in the scientific literature "black box" models are the well-known regression equations (e.g. polynomials) used to fit data by the method of the "least squares". Such type of models have been utilized in the modeling of FI systems and allow some quantities of interest to be calculated for various sets of selected independent parameters of the systems using multiple regression analysis, These quantities of interest might be: the dispersion coefficient of Ruzicka et al. [6-7]; the peak height in the case of isocratic [8] or gradient [8] flow; the travel time [9]; the baseline-to-baseline time [10-11]; the appearance time of the maximum [7]; the dispersion volume [8]; the plateau width in the case of large sample volumes and non-reacting analyte or the time between peak maxima at both interfaces of a large reacting sample plug [12]; the rate of dilution in open-closed [13] and flow-reversal [14] systems; the peak area [15]; a linear combination of peak height and mean residence time used as a response function in the experimental optimization of FI systems [16], the peak width in flow-reversal titrations [17]; and the axial dispersion coefficient [18].

Artificial neural networks

Recently an advanced artificial intelligence technique known as the artificial neural networks approach has been successfully applied for the modeling of FI systems with photometric [19] and ion selective electrode array [20] detection. The modeling process is performed by a net of interconnected processing units (neurons). Every neuron receives a number of input signals which are weighted and summed. Then the result obtained is further operated by the transfer function of the neuron yielding an output signal which is confined in the interval between 0 and 1. By increasing the number of neurons up to a certain extent, above which the network starts to learn the noise, the predictive power increases. Unfortunately this is accompanied by extensive increase in the computation time required for training the network and this is in fact a limitation for the neural network approach in the modeling of FI systems.

Impulse-response functions

All the "black box" models discussed above consider the whole FI system as one indivisible module thus neglecting the individual influence of the main sections of the system on its overall behavior. For this reason it is difficult to extend the results obtained to other even similar flow configurations. In a series of papers Van Nugteren-Osinga et al. [21] have shown that it is much more advantageous to apply the "black box" principal to the main individual flow-through sections of a given FI manifold than to the system as a whole. This task has been performed by calculating the impulse-response function of different FI sections, (e.g., coiled and knitted tubes, mixing T-pieces [21], various measuring cells [22]) by means of a de-convolution procedure of the response curves of a given FI system obtained with and without the section concerned.

Statistical moments and special functions

The flow pattern in FI manifolds can be characterized by the concentration curve, $c(t)$, monitored in the measuring cell which is frequently termed as peak in analogy with chromatography. In the absence of chemical interactions this curve gives information about the fraction of the fluid that spends a certain time in the manifold and can be defined as the residence time distribution function [23]. Since the specific details of the history of movement of fluid throughout the manifold are not necessary for calculating the moments of the peak this approach can be referred to the "black box", principle. However, the residence time distribution function and its moments can provide useful information about the pattern of flow, e.g., molecular diffusion and convection effects, the existence of dead spaces, bypassing or non-uniform regions [24]. The moments which are most important and frequently used for characterization of peaks are the first moment about the origin, μ_i for $i = 1$, and the second moment about the mean, σ^2. The former moment, known as the mean, defines the center of gravity of $c(t)$ while the latter one, known as the variance, characterizes its width [25].

$$\mu_i = \int_0^\infty t^i c(t)dt / \mu_0 \qquad (1)$$

where t is time, C is concentration (mol m^{-3}) and d is diameter.

$$\sigma^2 = \int_0^\infty (\mu_1 - t)\, c(t)\, dt\, /\, \mu_0 = \mu_2 - \mu_1^2 \qquad (2)$$

The quantity μ_0 is the zeroth moment which multiplied by the volumetric flow rate gives the injected amount provided no sources and sinks are present in the manifold.

$$\mu_0 = \int_0^\infty t^i c(t)\, dt \qquad (3)$$

The statistical moments of experimentally measured peaks can be calculated by direct numerical integration, by the Edgeworth-Cramer method, or by relationships between the moments and other directly measurable peak characteristics (e.g., area, height or width at various heights) assuming a priori that the residence times of the fluid elements obey a certain law of distribution (e.g., Gaussian distribution). The numerical integration is straightforward and easy to implement especially in the case of computer data acquisition.

Statistical moments can be determined also if the experimental peak is subjected to nonlinear least-squares fitting to a truncated Edgeworth-Cramer series [26].

For large mean residence time (t_m) the $c(t)$ curve approaches a symmetrical Gaussian distribution curve, $G(t)$, around t_m (Eq. 4) and the following equality holds equality holds $\mu_1 = t_m$ [24].

$$G(t) = \frac{A}{\sigma\sqrt{2\pi}} \exp\left[-\left(\frac{t - t_m}{\sqrt{2}\sigma}\right)^2\right] \qquad (4)$$

where A is the peak area and σ is the peak standard deviation. The variance in this case can be related directly to the peak width [27].

Analytical-experimental models

An analytical-experimental model is built by uniting the mathematical descriptions of the flow pattern, the heat- and mass-transfer and the kinetics of the chemical reactions in the modeled system. In some cases only fundamental physical constants and directly measurable parameters (e.g., geometrical dimensions, flow rate) are used and the corresponding models are known as models

based on first principles. However, very often the analytical-experimental models include parameters (e.g., axial dispersion and mass-transfer coefficients) which in most of the cases can be determined only on the basis of experimental data. Usually the development of an analytical-experimental model requires a large amount of information for the system it describes and its solution is frequently accompanied by serious mathematical and computational difficulties. However, once built and solved the model can be used for simulation and optimization of the system it describes. Unlike "black box" models its application usually is not confined within the region of experimental data used for identification of the parameters of the model.

Probabilistic models

Random walk models. Models of FI systems based on the random walk simulation approach [28] can be referred to as probabilistic models. After a successful utilization in the modeling of chromatographic processes this approach has been used both qualitatively [29] and quantitatively [28] for the description of single-line systems with constant [28] and sinusoidal [29] flow rates, and for systems with merging zones [30]. The random walk model considers the sample plug as a discrete number of individual molecules and the time interval of observation as consisting of a certain number of subintervals (Δt) of equal duration. During each subinterval, each molecule is transported down- stream by convection (e.g., laminar flow) and then takes a random step in x, y or z direction $\Delta l = (2D_m\Delta t)^{1/2}$ where D_m is the molecular diffusion coefficient.

Deterministic models

In the majority of the models of FI systems, describing the behavior at macro level, each variable and parameter can be assigned a definite fixed number, or a series of fixed numbers, for any given set of conditions. For this reason those models fall into the group of the so-called deterministic models [31]. Most of them have been introduced in chemical engineering for the mathematical modeling of the physical and chemical processes taking place in various flow-through equipment. They could be classified in

accordance with the independent variables they incorporate into distributed- and lumped-parameter models [31] (Fig. 1). For simplifying the mathematical solution when these models are used, for the mathematical description of Fl systems the sample injection has been very often approximated by a delta-function input. The solution of the model under this assumption can be related very easily to the solution of the model in the case of step-function input which is not typical for FI applications, i.e., $C_{delta} = dC_{step} / dt$.

Distribution parameter models (dispersion models).

The dispersion models (Table-1) take into account detailed variations in behavior from point to point throughout the system. These models are represented by the so-called distributed-parameter models which are based on the analogy between mixing in actual flow and a diffusion process and as a result of this they use diffusion equations with modified diffusion coefficients [32]. In chemical engineering these models are useful mainly to represent flow in empty tubes and packed beds, which is much closer to the ideal case of plug flow than to the opposite extreme of back mix flow [33-35]. Only two dispersion models have been utilized in the mathematical description of FI systems so far. These are the uniform dispersion model with radial and axial dispersion coefficients equal to the molecular diffusion coefficient and the axially dispersed plug flow model (Table-1).

Table 1. Dispersion models

Name of the model and defining differential equation	Parameters
General dispersion model $$\frac{\partial c}{\partial t} = \nabla(D\nabla c) - U\nabla c + s$$	$U = U(x, y, z), D = D(x, y, z)$
General dispersion model for symmetrical tubular flow $$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D_L \frac{\partial c}{\partial x} + \frac{1}{r}\frac{\partial}{\partial r}\left(rD_R \frac{\partial c}{\partial r}\right) - U\frac{\partial c}{\partial x} + s$$	$U = U(r), D_L = D_L(r), D_R = D_r(x)$
Uniform dispersion model $$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} + \frac{D_R}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) - U\frac{\partial c}{\partial x} + s$$	$U = U(r), D_L = const., D_R = const.$
Dispersion plug flow model $$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} + \frac{D_R}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) - U\frac{\partial c}{\partial x} + s$$	$U = const., D_L = const., D_R = const.$
Axially dispersion plug flow model $$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - U\frac{\partial c}{\partial x} + s$$	$U = const., D_L = const.$

Uniform dispersion model

The uniform dispersion model takes into consideration the real velocity profile and thus it will differ for flow-through sections with different geometry. In FI systems the most frequently encountered flow-through elements with simple geometry are straight and bent or helically coiled open tubes and flow-through sections with parallel plate flow (e.g., parallel plate flow-through measuring cells and dialyzers). The mathematical description of the dispersion process in them based on first principles will be considered in the subsequent paragraph.

Straight open tubes with circular cross-section

For straight open circular tubes with fully developed laminar flow the uniform dispersion model reduces to the well-known convective-diffusion equation in cylindrical coordinates (Eq. 5).

$$\frac{\partial c}{\partial t} = D_m\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) - 2\mu\left(1 - \frac{r^2}{a^2}\right)\frac{\partial c}{\partial x} \quad (5)$$

where u is the mean linear flow rate in. the cross-section of a tubular flow with radius a; x and r are the axial and radial coordinates, respectively; the flow remains laminar for values of the Reynolds

number, $Re\ (=2au/v$, where v is the kinematics viscosity), up to 2100 [36].

Vrentas and Vrentas [37] have developed an asymptotic solution valid at arbitrary τ for sufficiently low Pe_R and at arbitrary Pe_R for sufficiently low τ. On the other extreme, i.e., at high Pe_R and τ, is the solution of Westhaver [38] and Taylor [39] obtained under the assumption that the dispersion process is diffusion controlled and the axial diffusion is negligible. Under such conditions Eq. 5 is reduced to the much simpler from mathematical point of view axially dispersed plug flow model (Table-1) with axial dispersion coefficient (D_L) defined by Eq. 6 (Table-2).

Aris [40] as extended the Taylor's theory for the case when the axial diffusion must be taken into account (Eq. 7 Table-2). It should be noted that the flow conditions encountered in FI systems are such that $D_m \ll a^2u^2/48D_m$ and Eq. 7 (Table-2) is indistinguishable from Eq. 6 (Table-2).

Table 2. Equations for the axial dispersion coefficient in laminar flow in open straight circular tubes.

Eq.	D_L	Ref.
6	$a^2u^2/(48D_m)$	34, 39
7	$D_m + a^2u^2/(48D_m)$	40
14	$1.314(D_L)_{Taylor}\tau^{0.55}$	54
15	$1.314(D_L)_{Taylor}\tau^{0.495}$	Present study

Axially dispersed plug flow model (ADPFM).

As the simplest dispersion model from a mathematical point of view the ADPFM (Table-1. has been widely used in the modeling of process and analytical flow-through (e.g., FI and chromatographic) systems. However, t should be pointed out that this model is best suitable for patterns of flow where the radial variation n composition is relatively small. For a limited number of initial and boundary condition (e.g., open system and open-closed system in the cases of step- or delta-function input) analytical solutions can be obtained [23-24].

To increase the generality of the results, the ADPFM (Table-1) is usually used in dimensionless form, i.e.

$$\frac{\partial c}{\partial \theta} = \frac{1}{Pe}\frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} + S \tag{8}$$

where θ, X and C are the dimensionless time, axial distance and concentration, respectively, $Pe = uL/D_L$ is the traditionally used in chemical engineering length based Peclet number which characterizes the dispersion properties of the system, and S is the dimensionless source and (or) chemical reaction term.

In the mathematical description of FI systems by the ADPFM, the flow system has been usually assumed as infinitely long (i.e., open vessel) and in most of the cases the introduction of the sample has been approximated by an ideal delta-function input, Eq. 9, [4, 5, 41-42].

$$\delta(\theta) = \begin{cases} \infty \text{ for } \theta = 0 \\ 0 \text{ for } \theta > 0 \end{cases} \tag{9}$$

Under these oversimplified boundary and initial conditions the solution of Eq. 8 is the following:

$$C = \frac{1}{2}\left(\frac{Pe}{\pi\theta}\right)^{1/2} \exp\left[-\frac{Pe(X-\theta)^2}{4\theta}\right] \tag{10}$$

The Peclet number or the axial dispersion coefficient can be directly related to the height equivalent to a theoretical plate (HETP) or simply the plate height (H) by the following relationships [43]:

$$Pe = 2L/H$$

and

$$D_L = Hu/2 \tag{11}$$

It should be pointed out that Eq. 10 is valid only if the sample volume is very small compared to the reactor volume [11]. Otherwise the sample injection should be approximated by a rectangular function which is obviously a more realistic approximation.

The corresponding analytical solution of Eq. 8 in this case is the following [44]:

$$C = \frac{1}{2}\left\{erf\left[\frac{\theta - X}{2(\theta/Pe)^{1/2}}\right] + erf\left[\frac{X + \alpha - \theta}{2(\theta/Pe)^{1/2}}\right]\right\} \tag{12}$$

where α is the dimensionless length of the initial sample plug.

The models based on the "open vessel" assumption do not take into account the fact that in reality even the simplest Fl system consists of various flow-through sections (e.g., fore- and after-sections, injection device, reactor, measuring cell) with different geometrical and dispersion properties. To overcome this serious drawback a mathematical model considering the flow system as consisting of several connected in series tubular sections with their own Peclet numbers has been developed by Kolev and Pungor [10]. This fluid system is described by a set of partial differential equations similar to Eq. 8.

$$\frac{\partial C_i}{\partial \theta} = \frac{\psi_i}{Pe_i}\frac{\partial^2 C}{\partial X^2} - \psi_i \frac{\partial C_i}{\partial X} - S_i \cdots \quad (13)$$

where ψ_i are coefficients [45] which make possible the use of Eq. 13 for the description of flow systems comprised of tubular sections with various diameters and c_i refers to the concentration in the ith flow section. The boundary conditions of Eq. 12 are those of Wehner and Wilhelm [46]. The source terms and the initial conditions allow to take into account several methods of sample introduction (i.e., syringe and hydrodynamic injection [47] or injection valve). The model can describe analyte detection in the measuring cell by surface (e.g., ion-selective [48] or enzyme [49] flow-through electrodes) or volume (e.g., conductimetric [50] detection) detectors. The generality of the model outlined above allows the study of the influence of the main parameters of single-line FI systems on the output signal to be performed by model simulations [51].

The ADPFM has been successfully used for the mathematical description of not only single line FI systems but of multi-channel flow systems as well. A mathematical model has been developed by Kolev and Vander Linden [52]. It takes into account the geometrical dimensions and the dispersion properties of the main sections of the manifold, the mass transfer in the channels of the separation module and the characteristics of the membrane (thickness and diffusion coefficient within it). Because of its generality the model can be used for improving the performance of FI systems with membrane separation modules. Other possible applications of the model are in membrane technology and process engineering for characterizing of various membranes and for investigating the mass transfer in different dialysers. The absolute limits of mass transfer across the membrane in a parallel-plate dialyser set by the flow pattern in both channels have been also determined on the basis of the model mentioned above [53].

Straight tubes

Ananthakri-shnan et al. [54] have fitted numerical results for various sets of values of τ and Pe_R by the axially dispersed plug flow model thus defining the regions of applicability of Eqs. 6 arid 7 (Table-2). An empirical relationship for D_L in a τ - Pe_r region where the Taylor-Aris theory does not hold (i.e., $\tau < 0.6$) has been obtained (Eq. 14, Table-2). For convenience the axial dispersion coefficient is related to the theoretical equation of Taylor, i.e., $(D_L)_{\text{Taylor}}$ (Eq. 6, Table-2). The predictions of Eq. 14 (Table-2) have been compared with experimental results reported elsewhere [55-56] (Fig. 2). An empirical equation similar to Eq. 6 with slightly different coefficients (Eq. 15, Table-2) offers a better agreement with the same experimental data (Figure 2).
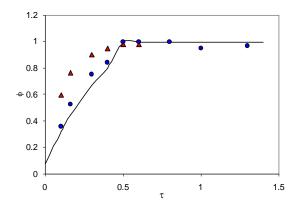

Fig. 2. φ vs. τ for laminar flow in straight open circular tubes. Experimental results: •, [55]; ▲, [56]. Calculated curves: 1 = Taylor's equation (Eq. 6), 2 = Eq. 14, 3 = Eqn. 15.

Tank-in-series model

The mathematical description of the tank-in-series model(TSM) in the case of N ideally mixed tank consists of N equations similar to equation

$$V_t \, dc / dt = V(c_o - c)]$$ (16)

in which the influent concentration of each tank is in fact the effluent concentration of the preceding tank. For simplifying the mathematical description process flow-through systems by the assumption for delta-function input has been usually employed [57].

$$c = [N \, (N\Theta)^{N-1} / (N-1)!] \exp(-N\Theta)$$ (17)

Such an assumption will hold only if the sample volume is much smaller than the reactor volume. This condition is rarely valid in FI systems and the finite volume of the sample must be taken into account. Reijin et al [58] have derived the corresponding solution of the TSM which is expressed in general case by two Chi-squared distribution functions. For large values of the number of tanks the Chi-square distribution can be approximated by Error function [59].

$$c = 1/2 c_o \{ erf[(N/2)^{1/2} (\Theta - 1) - erf[(N/2)^{1/2} (\Theta - \alpha - 1)] \}$$ (18)

Kolev et al (60) have empirically approximated the exact solution of the TSM with finite sample volume (Eq. 18) by multiplying the delta-function solution(Eq. 16) by α thus obtaining of much simpler than Eq. 12 expression. Such a simplification will be valid for $N^{1/2} \alpha < 1.4$ [57].

Application of Existing Flow-Injection Models for Environmental Monitoring

The mathematical models which described above can be useful for all types of FIA systems (e.g. FI, SI, BI, FIAAS, FI-HGAAS, SIA, PSA-FIA-AAS, FIA-ICP, FIA-MS).

The majority of the existing mathematical models outlined above view only single-line(SL) flow-injection systems with or without chemical reaction. Those system characterized by one influent and one effluent stream through which they contact with their environment. Generally speaking a SL FI system (Fig. 3a) can be considered as consisting of the following tubular sections connected in series or only of some of them[60]: (i) fore- and after-sections(e.g. tubes connecting the injection device with the reservoir of the carrier solution and the measuring cell with

the waste); (ii) injection section, usually an injection valve but may be a syringe or a hydrodynamic injection section as well; (iii) reactor, the flow-through section connecting the injection device with the detector. This section may incorporate a straight or coiled tube, packed bed, single-bead string, knitted, or imprinted geometrically disoriented reactor and some connecting tube as well (Figure. 3a); (iv) measuring cell.

If the method requires more than one reagent, additional streams can be merged with the carrier stream at suitable points in the manifold. Simultaneous FI can be performed by designing split line manifold in which the sample is injected into more than one flow channel and undergoes a different reaction in each channel. The manifold shown in (Figure 3b) is known as multi-channel system. This can be achieved either by splitting the carrier stream after injection or by connecting two injection valves in series in two separate reaction systems.

As has been already pointed out the most distinctive characteristic of such a system (conjugated two-line) is the existence of a flow-through section with two separate streams (donor and acceptor) which exchange matter (e.g. solute or solvent, or both of them) continuously along a common semi-permeable interface (e.g. membrane) (Figure.3c). Flow sections corresponding to such a description are the membrane separation modules for dialysis, gas diffusion or ultra-filtration incorporated in FI manifolds. Three different approaches have been utilized for the description of the simultaneously occurring processes of dispersion and mass exchange between the donor and the acceptor streams, i.e. the uniform dispersion model [61-62], the tanks-in-series approximation [63] and the axially-dispersed plug flow model [64-66].

On the basis of the considerations made above it can be concluded that three of the cornerstones in the modeling of FI manifolds are the successful mathematical description of single-line, multi-channel and conjugated two-line systems. Mathematical models of these three systems as well as of manifolds incorporating them outlined earlier will be discussed in view of finding

an appropriate model or combination of models offering an acceptable compromise between the contrary requirements for maximal possible mathematical simplicity and maximal possible precision.
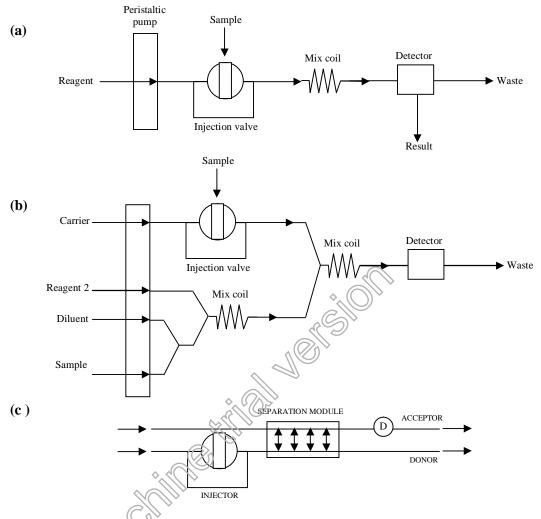

Fig. 3. Schematic representation of FI system. (a) Single-line system; (b) multi-line system; (c) conjugated two-line system

Experimental Section
Simultaneous determination of nitrite and nitrate in environmental water by FIA [67].

The aim of this study was to develop a simpler FI system for the simultaneous determination of nitrite and nitrate with 3-nitroaniline using a copper column before the copperized cadmium column in the reaction manifold. In this paper 3-nitroaniline (NA) is used as the azo component and N-(1-naphthyl) ethylenediamine dihydrochloride (NED) as the coupling component.

Apparatus

The manifold for the simultaneous determination of nitrite and nitrate was made of poly(tetrafluoroethylene)(PTFE) tube(0.8mm i.d.) and linear dual connector were used (Fig. 3b). It consisted of a four-way pneumatically actuated injection valve (Rheodyne, Type 50 Teflon, Cotati, CA), and eight-channel peristaltic pump(Ismatec, Glattburg-Zurich, Switzerland) and a filter spectrophotometer[62] equipped with a fiber optic for the transmission of the light from the source to the flow cell (2μL) for measurement. Data

processing and collection were performed with IBM-compatible PC by means of soft-ware written in Microsoft Q-Basic. The interface unit was an RTL 800 / 815 multifunction input/output board. A Shimadzu (Kyoto, Japan) Model UV 2100 double-beam UV / VIS recording spectrophotometer was used for comparison of the results.

Reagents and Solutions

All chemicals were of analytical-reagent grade or the highest purity available. A 100 mL of stock nitrite solution (1 mg mL^{-1}) was prepared by dissolving 492.8 mg dried sodium nitrite (Merck) in doubly distilled water. A 100 mL of stock nitrate solution (1 mg mL^{-1}) was prepared by dissolving 607.1 mg dried sodium nitrate (Merck) in doubly distilled water. The solutions were treated with a few drops of chloroform and kept in a refrigerator for preservation. Working standard solutions were freshly prepared by diluting the stock solutions with 0.4 M NH_4Cl.

Procedure

The standards (0.01 - 2.2 μg mL^{-1} NO_2^- or 0.1 – 3.5 μg mL^{-1} NO_3^-) and samples were injected into a carrier stream by means of the peristaltic pump, P (Figure 3b). The sample was then split into two streams using a selector valve. One of the streams was directly treated with acidic mixed reagent (2000- 10,000 fold molar excess) and passed to the sample flow cell of a spectrophotometer where the absorbance due to nitrite was measured at 535 nm. The other stream was passed through the reduction micro-column of copper (R_1) and copperized cadmium (R_2) column using a second selector valve where nitrate was

reduced to nitrite. The sample was then treated with the mixed reagent and the overall mixture was passed to the same cell of the spectrophotometer where the absorbance due to nitrite and nitrate was measured; nitrate was determined from the differences in absorbance values. The reaction was instantaneous and absorbance remains stable for 24 h. The mixed reagent (NA + NED) was colorless and did not show any absorbance.

Each filtered environmental water sample (45mL) was taken into a 50 mL calibrated flask and diluted to the mark with 0.4M NH_4Cl. The concentration of nitrite and nitrate in environmental waters were evaluated from the peak heights by using calibration curves prepared from standards.

Results and discussion

In order to optimize the proposed flow-injection manifold, the influence of the hydrodynamic and chemical parameters on the magnitude of peak height, the shape of the and the reproducibility of results was studied. Various analytical parameters, such as effect of acidity / pH, flow rate, sample size, dispersion coefficient, temperature, reagent concentration and interfering species were studied. The reliability of the procedure was tested by recovery studies. Environmental samples were analyzed by the proposed FIA method and by the standard AOAC method using sulfanilamide-NED. The results obtained are given in Table 3 and show that FIA method gives results very similar to the AOAC official method. The precision and accuracy of the method are very satisfactory.

Table 3. Determination of nitrate and nitrite in environmental water samples [67]

Sample	Concentration of nitrate (mgL^{-1})			Concentration of nitrite (mgL^{-1})		
	Method			Method		
	FIA	AOAC	Error (%)	FIA	AOAC	Error (%)
Tap water	2.01	2.01	0.00	0.01	0.01	0.00
River water	0.69	0.68	1.40	0.02	0.02	0.00
Spring water	20.4	20.2	0.98	0.01	0.01	0.00
Sa water	7.65	7.70	0.65	-	-	-
Lake water	1.73	1.70	1.70	0.05	0.05	0.00

Conclusions

The analytical-experimental mathematical models for single-line, multi-channel and conjugated two-line FIA systems developed and experimentally confirmed in the present work show the following three main advantages:

(1) They take into consideration the differences in the dispersion properties and the geometrical dimensions between the sections of the described flow systems.

(2) They consider various ways of analyte injection and detection.

(3) The models for FIA systems with detectors measuring the local or the average concentration are general also with respect to the type of the reactor used. The parameter identification procedure based on curve fitting can be utilized for the determination of the diffusion coefficients of the injected particles (e.g., ions, molecules) when the Taylor theory is valid for the reactor. The mathematical models outlined in this work could be used also for investigation of the flow pattern in chromatographic manifolds and in process systems composed of tubular sections. After the introduction of the necessary additional terms (e.g., chemical reaction terms, separation terms) in the equations comprising the models mentioned above, the models
can be applied for the description of flow analysis and process systems in the case of chemical reaction or for the modeling of the processes in chromatography.

Tank-in-series model(TSM) and the axially dispersed plug flow model (ADPFM) have gained considerable popularity in the description of not only process reactors but of analytical flow-through systems as well as. Their main advantage in comparison with the models discussed above is that at the expense of relatively limited mathematical and computational efforts they can describe satisfactorily patterns of flow between the two extremes of ideally plug and back-mix flow. As per as they do not require any prior knowledge on the exact velocity distribution in the system they can be applied without limitations to all types of flow-through comprising the existing in the

analytical practice FI manifolds. The TSM and the ADPFM have been successfully used for the modeling of all single-line, multi-channel and conjugated two-line systems.

FIA is a versatile technique. It is also a "milestone in analytical chemistry" [68]. Recently there have been considerable interests in process analytical chemistry, bio-analytical field, clinical chemistry, agricultural, pharmaceutical and environmental analysis. Therefore, the FIA systems should be successfully applied to the monitoring of trace amounts pollutants in environmental samples.

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