DECONVOLUTION OF FLOW ANALYSIS SIGNAL FOR CHEMICAL PROCESS INFORMATION RECONSTRUCTION


Abstract

Flow Injection Analysis (FIA) is an instrumental technique widely used in Analytical Chemistry (1) because allows the automation of manual operations. Nevertheless, there is not its counterpart in chemical industry, even if the technique could be easily implemented in chemical processes. Their use implies systematic calibrating work each time the operation conditions change (e.g. flow rate, etc.). When these conditions change frequently, as in an industrial environment, this operation should be repeated as many times the conditions have been changed. On the other hand, FIA could be also an interesting technique for continuous monitoring of dynamic chemical reactors. However, the coupling between axial convection and radial dispersion of the analyte implies a mathematical modelling of the dispersion phenomenon in the FIA system. This model let us relate the real concentration in the reactor with the concentration measured in the FIA detector (Fig 1), affected by dispersion, with applications in reactor monitoring or control.

In this work, the transfer function formalism is used to model FIA processes in combination with Tikhonov’s regularisation for chemical information reconstruction. This formalism has never been applied before in flow analysis systems. The advantages of obtaining kinetic information from chemical reactors and its possible use in process control are outlined.

From the one-dimensional dispersion model, a transfer function for the dispersion of the solute in the conduction can be obtained (2):

\[
h(p) = \exp(\alpha \cdot \beta - \alpha \cdot (p + \beta^2)^{1/2})
\]

that considers two dispersion parameters, \(\alpha\) and \(\beta\), which should be obtained from experiments.

Let us consider that the input signal, \(S(t)\), can be written as a linear combination of unit step functions:

\[
S(t_k) = S_0 + \sum_{i=1}^{k-1} \Delta S_i \cdot U(t_k - t_i)
\]

where \(S_0\) is the initial value of the input signal, \(U(t)\) is the unit step function and \(\Delta S_i\) are constants to be evaluated. Taking into account equations [1] and [2], after Laplace inversion, the measured response can be written as:

\[
R(t_k) = S_0 \cdot F_S(t_k) + \sum_{i=1}^{k-1} \Delta S_i \cdot F_S(t_k - t_i)
\]

where \(F_S(t)\) is the response of a unit step, obtained from equation [1]. Equation [3] can be rewritten as the following ill-conditioned system of linear algebraic equations:

\[
R = F \cdot \Delta S
\]

The matrix \(F\) is nearly singular, generating an unstable solution when conventional algorithms are used for the solution of [4]. Nevertheless, regularisation methods let us stabilise the solution by introducing additional information about that solution (3,4). In this work the Tikhonov’s regularisation method has been used. The idea is to obtain a solution \(\Delta S\) which minimises a weighted combination of the solution of the linear system, \(\|F \cdot \Delta S - R\|^2_2\), with the side constraint \(\|L \cdot (\Delta S - \Delta S^*)\|^2_2\):

\[
\Delta S = \min \left\{ \frac{1}{\lambda^2} \cdot \|F \cdot \Delta S - R\|^2_2 + \lambda^2 \cdot \|L \cdot (\Delta S - \Delta S^*)\|^2_2 \right\}
\]

where \(\lambda\) is the regularisation parameter, \(\Delta S^*\) is an initial hypothesis about the solution and \(L\) is the regularisation operator. This methodology has been applied successfully to the deconvolution of the signal registered by a FIA detector connected to a continuous stirred tank and a gas-liquid reactor, letting us the reconstruction of the information of the process, as can be seen in Fig 2. Different hypothesis about the evolution of the substance concentration in the reactor have been used as additional information.
Fig 1: Experimental set-up for continuous flow analysis

Fig 2: a) Typical measured response, $R(t)$, in a dispersion+Gas-liquid reaction experiment.  
b) Deconvolved data, $S(t)$, using different hypothesis.