Sequential injection analysis linked to multivariate curve resolution with alternating least squares

A. Pasamontes, M.P. Callao

This article discusses the potential of using sequential injection analysis (SIA) for generating second-order data. To treat these data, we used multivariate curve resolution with alternating least squares (MCR–ALS) as the chemometric tool. This combination can be used for both qualitative and quantitative analyses, since it provides concentration and spectra profiles for the various species. By combining these techniques (SIA–MCR–ALS), several analytes can be determined simultaneously in the presence of interferents without the need to pretreat the sample.

We describe the state of the art of both techniques by reviewing the literature since 2004 and the necessary conditions for applying chemometric tools to treat this type of data. We also discuss the advantages and disadvantages of this combined technique and examine the future prospects of SIA and MCR–ALS.

Keywords: Alternating least squares; MCR–ALS; Multivariate curve resolution; Second-order data; Sequential injection analysis; SIA

A. Pasamontes*, M.P. Callao
Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n (Campus Sescelades), E-43007 Tarragona, Spain

*Corresponding author.
Tel.: +34 9775 58122;
Fax: +34 9775 58446;
E-mail: alberto.pasamontes@urv.net

1. Introduction

Since Ruzicka and Hansen [1] introduced flow systems in 1975, many papers and reviews have used this technique, known as flow injection analysis (FIA) [2–8]. In 1990, Prof. J. Ruzicka [9] developed the second generation of flow systems, known as sequential injection analysis (SIA), in which the samples and reagents are introduced sequentially and with a double-flow direction. Table 1 lists the numbers of reviews and tutorials that indicate the popularity of this technique and its scope of application.

One characteristic of the sequential flow system is that the reagents mix with the sample *via* an interdiffusion process. Depending on the experimental conditions, after passing through the detector, the reagent will have interacted totally or partially with the analyte. If the reagent has interacted totally, the analyte (A) will be converted into the reaction product (P). However, if the reagent has interacted partially, the following areas will be observed as it passes through the detector:

- the analyte that did not react (A);
- a mixture of P and A; and,
- a reaction product (P).

This characteristic, together with the versatility of the system in coupling to different types of detectors, enables data of different dimensions to be obtained. This means that various chemometric tools can be used to provide information about the system.

Fig. 1 shows a scheme of the various possibilities. Figs. 1(a)–(c) represent a situation in which the chemical reaction has been completed before the sample passes through the detector. Figs. 1(d)–(f) represent a situation in which the chemical reaction is still taking place when the sample passes through the detector.

There are three types of detectors, depending on their ability to provide data independently. Some detectors provide single data (e.g., the photometer), some provide vector data (e.g., the diode-array spectrophotometer (DAD)) and others provide matrix data (e.g., the excitation–emission spectrofluorimeter). The signal obtained is that provided by the detector over time.

If the sample contains the same species, the only thing that changes over time is the concentration of the species due to the phenomenon of dispersion; the information obtained at two different times is the same. If, over time, different species pass through the detector, there is an effective change in the signal, which increases the dimension supplied by the detector by one.

0165-9936/$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.trac.2005.04.017

Table 1. Published reviews and tutorials about sequential injection analysis (SIA)

Focus	R/T	Number of references	Year	Ref.
Food analysis (wine)	R	21	2004	[10]
Food analysis	R	105	2005	[11]
Monolithic columns	T	75	2003	[12]
Multicommutation based on solenoid valves	R	51	2002	[13]
Operational parameters of SIA	T	112	1998	[14]
Operational parameters of SIA	R	301	2002	[15]
Pharmaceutical	R	54	2003	[16]
Process analytical chemistry	R	25	1999	[17]

For this reason, Figs. 1(d)–(f) have one more dimension than Figs. 1(a)–(c).

The study of chemical systems using data obtained by flow techniques and later subjected to chemometric treatment has highlighted the usefulness of such techniques [18]. Worth mentioning in this respect are those [19–22] with FIA and MCR–ALS. The aim of this article – i.e., to focus on one flow system (SIA) and one type of data treatment (MCR–ALS) – is to show the possibilities of SIA for generating this type of data, the conditions necessary for applying this chemometric tool and the advantages and disadvantages of this type of combination. We also discuss the state of the art of SIA and MCR–ALS by reviewing the literature since 2004 and examine their future prospects.

2. Sequential injection analysis (SIA)

The classical configuration of SIA is shown in Fig. 2. In a first step, a syringe pump aspirates the sample and the reagents *via* a valve that enables the desired reagent to be aspirated. In a second step, the syringe pump pushes the sample towards the detector through channels (in which the sample and reagents mix by dispersion) that join together the valve, the syringe and the detector. A computer controls the functions of every component.

The advantages of SIA are that it can be easily automated and miniaturized, the cycles can be executed repeatedly, it is highly versatile because it can be adapted to suit most analytical instruments, the frequency of analysis can be high and the consumption of samples and reagents is low. Thanks to these advantages, SIA has been used in a wide range of applications.

To illustrate the state-of-the-art of this technique, Table 2 shows some studies published since 2004. The most widely studied applications have been in the pharmaceutical, environmental, food and bioprocessing fields. The chemical species studied were very diverse and the detector most often used was UV–VIS. In practically all cases, the data were of the type shown in Fig. 1(a) – i.e., the chemical reaction was completed before it passed through the detector and a single datum was obtained per sample. In most cases, the sample was pre-treated.

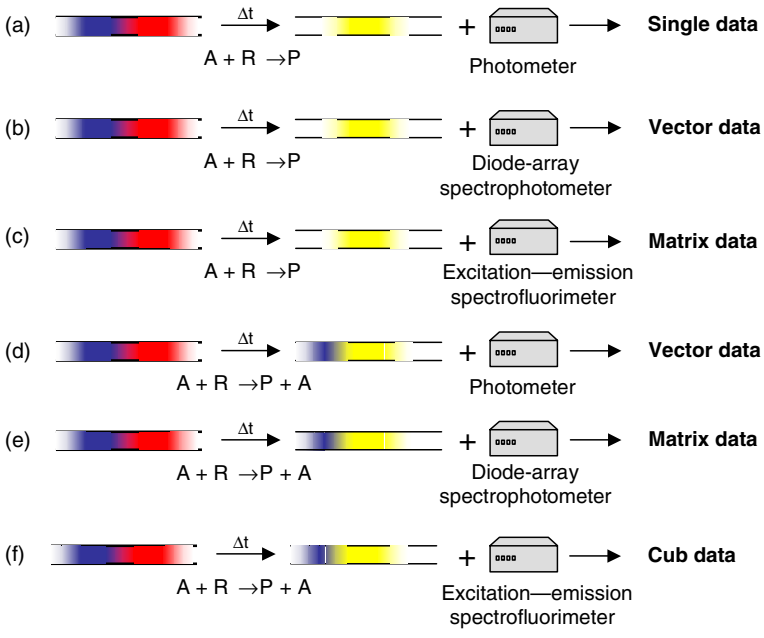

Figure 1. Scheme of the different types of data that can be obtained by a sequential flow system and different types of detector. A, Analyte; R, Reagent; P, Product.