Multisyringe flow injection analysis, a young and promising flow technique

Víctor Cerdà

Dep. Química. Universitat de les Illes Balears.
E-07071 Palma de Mallorca. Spain. E-mail: vcerda@p01.uib.es

Abstract

In the present work a brief introduction on multisyringe flow injection analysis (MSFIA) is carried out, including a description of the main characteristics of the system, advantages and inconveniences against other flow techniques, historical evolution and its different ways of performing.

Keywords: Multisyringe flow injection analysis, MSFIA.

Introduction

Since segmented flow analysis, proposed by Skeggs[1], which can be considered as the first flow technique, different variants have appeared, such as flow injection analysis[2] (FIA), sequential injection analysis[3] (SIA) and multicommuted flow injection analysis[4] (MCFIA)[5], each of them offering several advantages and inconveniences described in a critical review published in Talanta[6].

The most recent flow technique is the so-called multisyringe flow injection analysis (MSFIA), which was conceived with the aim to compile all the advantages of the former techniques, i.e., sampling rate of FIA, robustness, versatility and reagent saving of SIA, speed of the commutation valves of MCFIA, etc.

MSFIA set up

The system starts with an automatic burette usual for titrations, in which the motor propels simultaneously and solidarily several syringes which can be of different diameter, which will define its flows ratio (Figure 1). At the head of each syringe a rapid commutation three way solenoid valve is found, which allows the commutation between two inlet/outlet positions without stopping the burette engine.

Advantages and disadvantages of MSFIA against other flow techniques

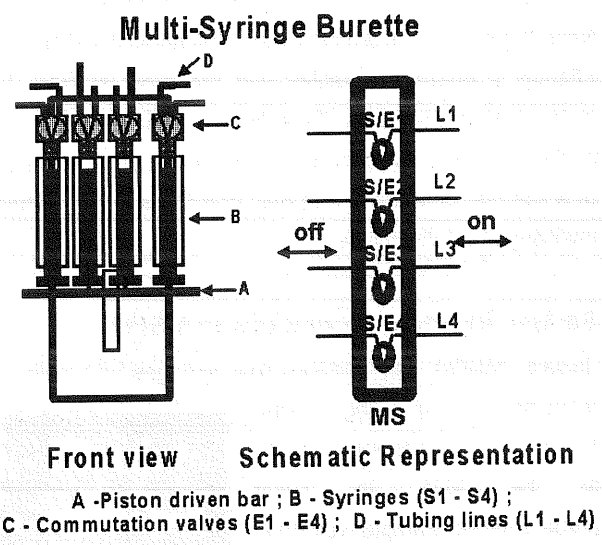

Figure 1. First MSFIA prototype

As above mentioned, MSFIA involves several advantages of the former flow systems.

On the one hand, carrying out the mixing of sample and reagents in parallel, allows to achieve the speed of FIA and its easiness in the mixing of fluids. In fact, the need to take a certain amount of time in loading the burettes makes this system slightly slower, disadvantage which may be overcome by the implementation of an additional burette which finishes the impelling of the sample segment up to the detector, while simultaneously the multisyringe is carrying out the loading

process. With this configuration, injection throughput of up to 200 per hour have been attained.

MSFIA does not possess, however, one of the great virtues of FIA -and which is unique to this latter technique against all the remaining techniques- consisting in the possibility of being applied without the presence of a computer. However, this is not totally an inconvenience for MSFIA and the remaining techniques, since the presence of a computer provides several advantages such as that of becoming very adequate for the stopped flow technique and, moreover, in the case of SIA and MSFIA, the advantage of only starting the system when measuring is required, thus, implying a considerable saving on sample and reagents. As in SIA, MSFIA has the great advantage of not requiring flexible tubes in the peristaltic pumps and, therefore, the liquids are only in contact with glass and Teflon, making these techniques especially robust in the handling of aggressive reagents and organic solvents.

MSFIA presents against SIA a significantly higher analysis rate due to the manipulation of liquids in parallel. Nevertheless, SIA is amidst all the flow techniques the one offering a greater versatility and the most suitable for multiparametric analysis. If a sufficient number of ports are at disposal, determination of all the significant parameters of a sample[7] is feasible with only one SIA system, without involving great difficulties.

Sample injection techniques in MSFIA

Initially, MSFIA only involved four syringes with solidary movement, implying the necessity of an additional device to be able to inject predetermined sample volumes. With this aim an additional module containing a rotary injection valve of traditional use in FIA was employed.

In the second prototype[8], two independent commutation solenoid valves were incorporated at the top of the multisyringe burette (Figure 2). By placing a Teflon coil between both valves, the additional module of the rotary valves was then not required, thus, making the system more compact, economical and versatile.

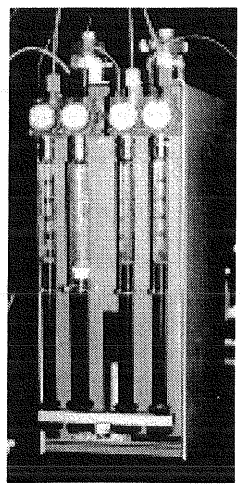

Figure 2. Second MSFIA prototype

The benefits introduced by these additional valves induced the creation of a third prototype in which versatility was enhanced by avoiding the pre-fixing of valves to be used and increasing the number of valves which could be controlled. For this purpose the valves located at the top of the module were eliminated and a lead was placed behind the latter, with four outlets, in such a way that each of them presents a commutable voltage of twelve volts. In each outlet up to three solenoid valves can be connected (or other devices which can be fed with this voltage). In this way, by using the same outlet, a synchronic commutation of several valves can be carried out (Figure 3).

Instead of using the system of a fixed load in a Teflon coil, requiring two solenoid valves and for each injection the process of loading the syringes, it is far more convenient to use the time based injection method. In this method only one commutation valve and a coil with a load large enough so as to contain sufficient sample to carry out three injections are required. This coil is located between the independent valve and that of a syringe (Figure 4). When the loading process is started, the coil is loaded with sample, so when the unloading process is carried out, the independent valve is commuted during a pre-fixed time. Consequently, an injection of a sample in the manifold -whose volume is proportional to the time in which the valve is found activated- will take place. In this way, with only one burette unloading three injections or more of the same sample are feasible to be carried out.

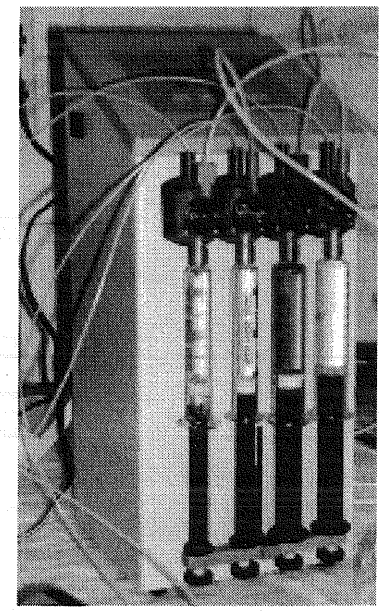

Figure 3. Third MSFIA version

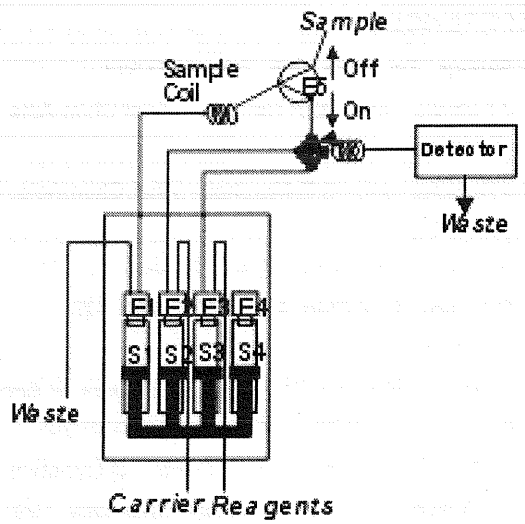

Figure 4. MSFIA setup for time based injection methods

In the fourth MSFIA generation a CCD spectrophotometric detector has been incorporated inside, in such a way that the whole analytical system happens to be integrated in the same module (Figure 5). This detector is able to obtain a spectrum between 200 and 850 nm with a minimum time of 5 milliseconds, which permits to attain a complete spectrum for each point of the MSFIAgram and, thus, correct the Schlieren effect and apply the chemometric techniques of multivariate analysis. The burettes and solenoid valves are controlled through a double RS232C interface, allowing the construction of a complete system with other detectors (pH, ISE, conductimeter, autosampler, etc) by only occupying one serial interface of the computer. The spectrophotometer is controlled through an USB interface, by which it is also fed. In this way, this module together with a computer (notebook) constitutes a very portable flow analytical system[9].

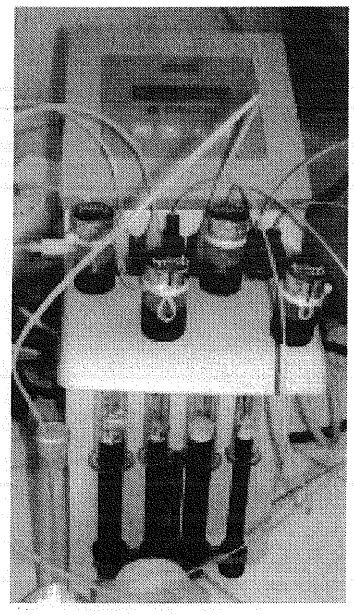

Figure 5. Forth MSFIA versión, with a valve platform and a CCD spectrophotometer inside

SIA-MSFIA systems

The last multisyringe generation system has proved to be very versatile, since combined with another valve module provided with two selection valves allows the implementation of double and simultaneous sequential injection system (Figure 6). This double system has been employed by our research group to develop a multiparametric monitor for the quality control of waters used in the co-generation of energy, with which all the significant parameters of a sample can be analysed every 30 minutes (pH, conductivity, acidic conductivity, phosphates, silicates, hydrazine, ammonium and iron). In this double SIA system each selection valve is used connected to a pair of syringes of the multisyringe burette, allowing a better mixing of liquids in parallel.

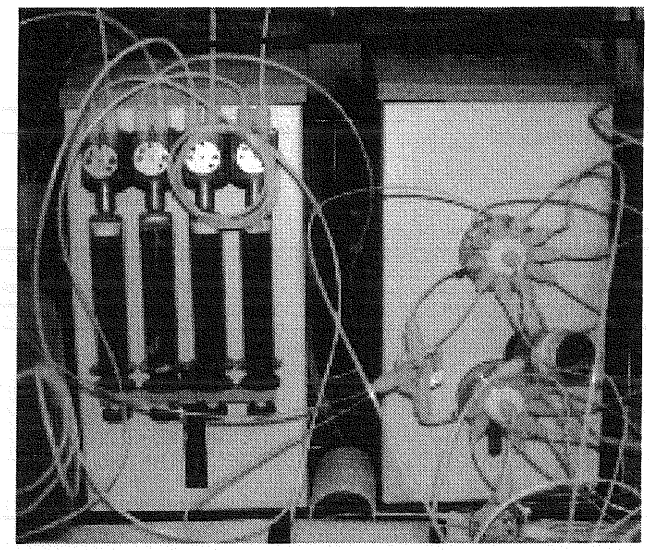

Figure 6. Double and simultaneous SIA system, constituted by a Multisyringe burette and a valve module provided with two selection valves

Another way of combining SIA with a multisyringe burette is based on the use of a SIA conventional system, composed of its burette and a valve module, with which the versatility present in SIA -involving the performance of very different operations- is added. Once the previous manipulation of the sample has been carried out, it is then impelled towards the multisyringe burette, where the mixing

process of sample and reagents is accomplished, with further detection of the formed products.

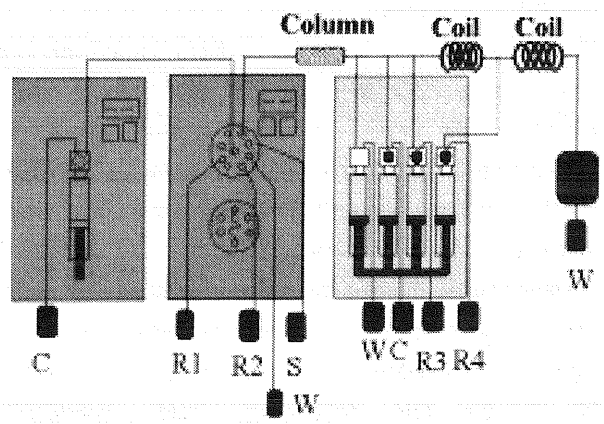

Figure 7. SIA-MSFIA system. The SIA components (in dark gray) are used for the sample pretreatments, whereas the MSFIA module is used for the final sample treatment and detection.

Acknowledgements

Most of the research on MSFIA has been carried out under financial support of the MCyT (Spanish Ministry of Science and Technology), project PPQ2001-0474

REFERENCES

[1] Skeggs. Am.J.Clin.Path., 28 (1957) 311

[2] J.Ruzicka and E.H.Hansen. Anal.Chim.Acta, 78 (1975) 145

[3] J.Ruzicka and G.D.Marshall. Anal.Chim.Acta, 237 (1990) 329

[4] B.F.Reis, M.F.Giné, E.A.G.Zagatto, J.L.F.C.Lima, R.A.Lapa. Anal.Chim.Acta, 293 (1994) 129

[5] J.Ruzicka. Analyst, 125 (2000) 1053

[6] V.Cerdà, J.M.Estela, R.Forteza, A.Cladera, E.Becerra, P.Altimira and P.Sitjar. Talanta, 50 (1999) 695

[7] O.Thomas, F.Theraulaz, V.Cerdà, D.Constant and Ph.Quevauviller. Trends in Anal. Chemistry, 1997, 16

[8] J.Klimundova, R.Forteza and V.Cerdà. Intern.J.Environ.Anal.Chem., 83 (2003) 233

[9] SCIWARE. www.sciware-sl.com

(Received September 17, 2003)

(Accepted October 1, 2003)