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Flow techniques in water analysis

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Abstract

In the present work the main flow techniques for the analysis and monitoring of several parameters of interest in the quality control of different types of waters are reviewed. Firstly, a review involving the advantages and disadvantages of flow techniques, from those currently out-dated, such as segmented flow analysis (SFA), to the most modern techniques, such as flow injection analysis (FIA), sequential injection analysis (SIA) and multi-commutation techniques (MCFA), is carried out. On the other hand, a new technique, the multi-syringe flow analysis (MSFA) is hereby described for the first time as both a fast and robust alternative. Its possibilities, limitations and potential advantages when using this technique either on its own or coupled to SIA, which carries out a previous sample handling, are outlined.

Keywords: Quality control; Waters; Syringe

1. Introduction

The acceptance of the existence of a correlation between environmental preservation and standard of living has led to the need of a vigilance and continuos control of a large number of environmental parameters. In this way new analytical methods — fast, robust and whenever possible multiparametric — capable of undergoing analysis of a large number of samples within a short period of time have been set up.

One of the current trends in the analysis of environmental parameters involves avoiding sampling in which all the samples are required to be carried to the laboratory. Thus, the use of screening methods, which may not be very selective, allow, however, the detection of alarm situations and, therefore, the most complete analyses are only carried out in those samples where eventually analysis is required.

Having to dispose of methods applicable to measurements in the open country, implies a change of the analyst's mentality, excessively used to very sophisticated and expensive techniques, their use being difficult to adapt outside the laboratory. On the other hand, this problem requires the use of robust techniques without demanding the continuos presence of the analyst, especially if they are applied to a continuos monitoring and/or

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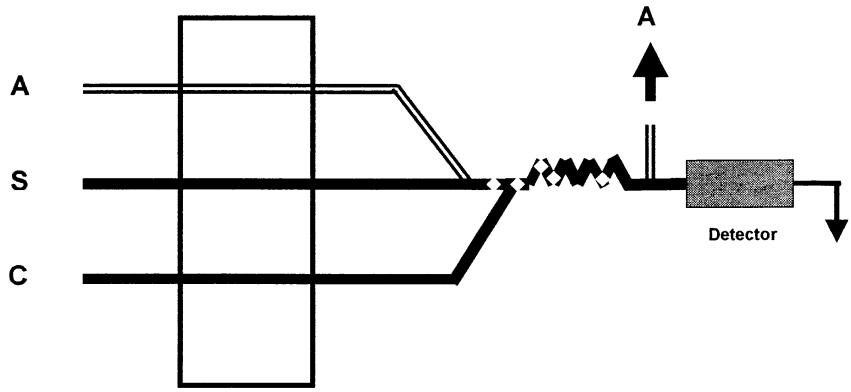

Fig. 1. Segmented flow system.

with very frequent measurements, in which, besides, reagent consumption for the performance of the analytical essays is not required or minimized. In order to be consistent with the aim of an environment quality improvement these reagents should be also environment-friendly.

Although for the analysis of certain environmental samples all the above-mentioned objectives are difficult to be achieved in a completely automatic way, aqueous samples are especially well adapted to be analysed by flow techniques. The advantages and disadvantages of each of the former techniques are reviewed below.

The importance and interest of these flow techniques regarding the study of water quality is reflected by numerous reviews which have been carried out within this field [1–18] either with a general approach, or in the case of their application to the determination of certain parameters. A vast majority of these works are referred to the application of flow injection analysis (FIA), which has been -by large- imposed during the last decades over the remaining techniques. There are hardly any bibliographical reviews worth to be mentioned regarding the other techniques, because of the fact that either they are no longer in use (SFA) or they have not been sufficiently developed yet (MCFA and MSFA). The only bibliographical review on SIA which we are aware of has been very recently published [19].

2. Techniques

2.1. Segmented flow analysis (SFA)

Segmented flow analysis was one of the first techniques widely imposed in the laboratories requiring a large volume of analysis, such as hospitals and oceanographic laboratories. The continuous segmented flow analysis methods (SFA), commercialized by the trade Technicon by the name Autoanalysers, are the classic methods described by Skeggs in 1957 [20] (Fig. 1).

Samples are sequentially aspirated and between them air bubbles are located which separate (segmentate) the flow established, including a washing cycle. Usually, the air bubbles are eliminated before reaching the detector flow cell. They frequently consist in multichannel techniques, in which there is an individual detector for each

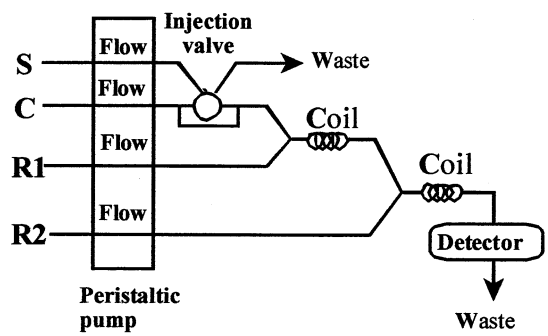

Fig. 2. Flow injection system.

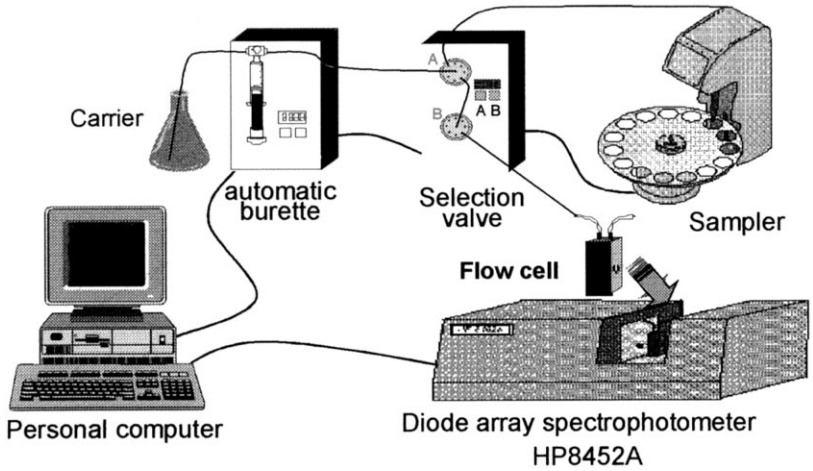

Fig. 3. Sequential injection system.

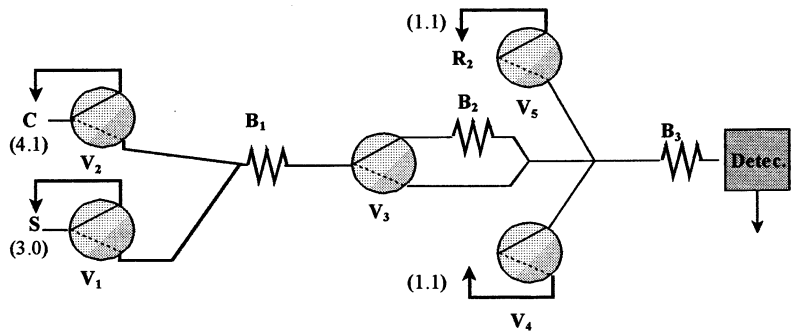

Fig. 4. Flow diagram of a multicommutation system for automatic single stage dilutions.

parameter to be determined, and therefore are usually expensive, although they offer good possibilities of working capacity. They have been designed to simultaneously determine even more than 20 parameters. These systems were gradually phased out by discontinuous automatic systems, until flow injection analysis (FIA) was introduced (Fig. 2).

Among the technical characteristics of SFA are the following: aspirated sample volumes 0.2–2 ml; response time 2–30 min; tube diameters 2 mm; detection in homogeneous equilibrium state; sampling frequency of up to 80 samples h^{-1}, precision of 1–2%, high reagent consumption and

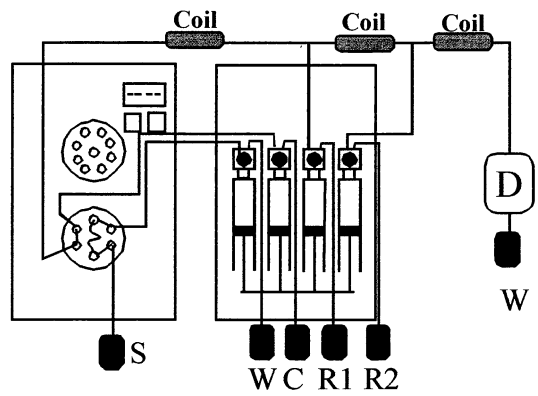

Fig. 5. Multisyringe flow system.

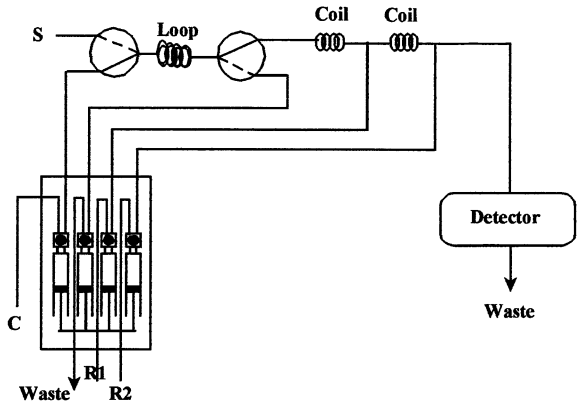

Fig. 6. Improved multisyringe flow system with sampling set up.

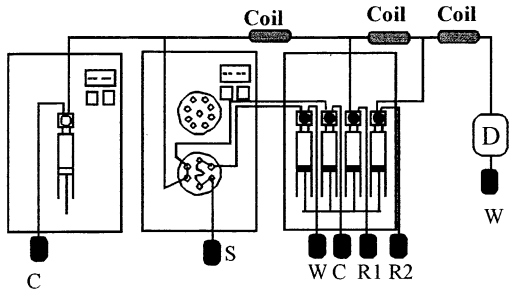

Fig. 7. Multisyringe flow system with additional burette.

essential washing cycle.More recently, microsegmented techniques for water analysis have been proposed [21–23].

2.2. Flow injection analysis (FIA)

The designation of flow injection analysis (FIA) [24,25] was proposed in 1975 by J. Ruzicka and E. Hansen. The inclusion of the term 'injection' in the name of this technique is due to more a historical aspect rather than the present situation. In the beginning of the former technique a syringe was used to inject a sample through a septum into a reagent flow. Nowadays, rotation valves which insert the sample into a flow of reagents, rather than injecting the sample, are used.

Although schematically and conceptually FIA and SFA may appear to be very similar, however, the differences in practice are remarkable. In the first place, in FIA, samples are not segmented by air bubbles and tubes are considerably narrower (of the order of 0.5–0.7 mm of i.d.), through which the flow pattern is of the laminar type. The injected sample volume in SFA is considerably larger than that of FIA, in which only volumes of the order of 10–100 ml are used. The response time is of 3–60 s, the frequency may well be of 120 samples h^{-1}, a similar precision to that of SFA (1–2%) is achieved, reagent consumption

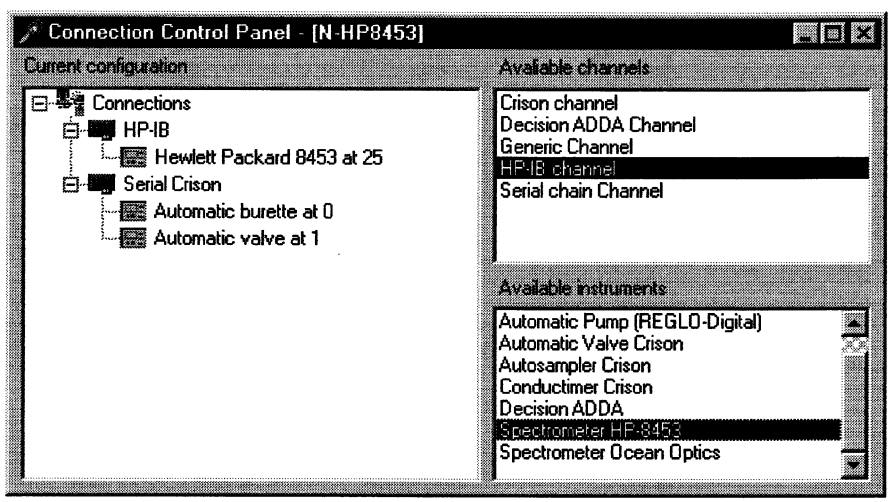

Fig. 8. Connection control panel for the AUTOANALYSIS program.

Table 1
Devices which can be controled with the AUTOANALYSIS program

Device	Function	Model	Firm
A/D 14 bits	16 channels	Super ADDA 14	Decision
A/D 8 bits Card with automatic gain adjustement	4 channels	SilMon Scope	Silmon
A/D 12 bits	8 channels	DASH8	Keithley
A/D 12 bits	8 channels, progr. Gain	DAS 801/CE	Keithley
I/O digital Card	48 lines 3 counters 16 bits 8255–8253		Decision
I/O digital Card			Flytec
I/O Card	16 Photo 16 reles	Industrial Smat-Lab	Decision
Peristaltic pump	Direct and reverse control, 4 channels	Reglo-Digital	Ismatec
SIA system	2 burettes, 2 analogic inputs, 1 selection valve+autosampler	Compact Titrator	Crison
Automatic burette	5000 steps	Microbur 2031	Crison
Automatic burette	1000 steps	Modelo 738	Crison
Automatic burette	4 syringes+2 commutation valves		Crison
Valves module	2 selection valves, 8 channels each	Pump 2060	Crison
Valves module	1 selection valve 8 channels, 1 injection valve 6 canales	Pump 2060	Crison
Valves module	1 selection valve 6 channels, 1 injection valve 6 canales		Sciware
Autosampler	40 samples	Microsampler 2040	Crison
Autosampler	15 samples		Crison
Microwaves oven	Needs DASH8 or DAS801 card	Maxidigest	Prolabo
Conductimeter		Digilab 517	Crison
Conductimeter		Modelo 525	Crison
Conductimeter		GLP 32	Crison
pH meter	Only pH	517	Crison
pH meter	pH and temperature	MicropH 2002	Crison
pH meter	pH and temperature	GLP22	Crison
Diode array spectrophotometer	190–800 nm	HP8452A	Hewlett-Packard
Diode array spectrophotometer	190–1100 nm	HP8453	Hewlett-Packard
CCD array fiber optic spectrophotometer	Master	PC1000	Ocean Optics
CCD array fiber optic spectrophotometer	Master	PC2000	Ocean Optics
CCD array fiber optic spectrophotometer	Slave	PC2000	Ocean Optics
Fluorimeter	Flurimetry for single point, synchronous, variable angle spectra	LS50	Perkin Elmer
Fluorimeter	Flurimetry for single point, synchronous, variable angle spectra	LS5	Perkin Elmer
Atomic fluorescence	Hydrides generator	Excalibur	PSA Analytical
SIA system	2 burettes, 1 slection valve, 2 A/D inputs	Compact Titrator	Crison

drastically decreases, the washing cycle is not required and the application of kinetic methods is feasible, with or without stopped-flow. The numerous advantages of FIA justified the fact that at that moment the continuous flow analysis methods were revitalized. However, undoubtedly, perhaps the major advantage is the great reproducibility in the results obtained by one

technique which can be set up without excessive difficulties and at very low cost of investment and maintenance. These advantages have led to an extraordinary development of FIA, not comparable to that of any other technique.

Nevertheless, to the former advantages a series of disadvantages are opposed, which are especially evident when used in the monitoring of environmental parameters. Undoubtedly, the Achilles' heel of this technique is the use of peristaltic pumps. The flexible tubing which these pumps require imply a change in both the sample and reagent flows in the short or long term due to tube squashing, which in turn implies a recalibration of the system. These tubes become especially vulnerable when management of relatively aggressive reagents is required, such as moderately concentrated acids or bases, or — especially — when handling organic solvents to improve solubilization of compounds or carrying out extraction processes. On the other hand, although several methods which allow the simultaneous determination of different parameters have been developed, the FIA technique is basically monoparametric, being also relatively limited when carrying out sample pre-treatments. In any case, FIA is one of the most preferred techniques in the determination of a parameter in a set of a large number of samples.

2.3. Sequential injection analysis (SIA)

Sequential injection analysis has been also proposed by J. Ruzicka et al. in 1990 [26] (Fig. 3). It consists in a conceptually simple technique and was initially proposed as a possible alternative to FIA. In practice, it has been proved that it offers very different possibilities, with a series of advantages and disadvantages in relation to the former. Initially, the use of sinusoidal propelling pumps difficult to program was proposed, however, subsequently, other alternatives have been introduced such as the same peristaltic pumps used in FIA [27], or the burettes used in automatic tritations [28]. The latter were initially limited by the still high rates at which they performed even at their lowest range rates (values >2 ml min^{-1}). Subsequent modifications in the firmware introduced by the manufacturer have allowed to solve the problem. Automatic burettes as an advantage elimi-

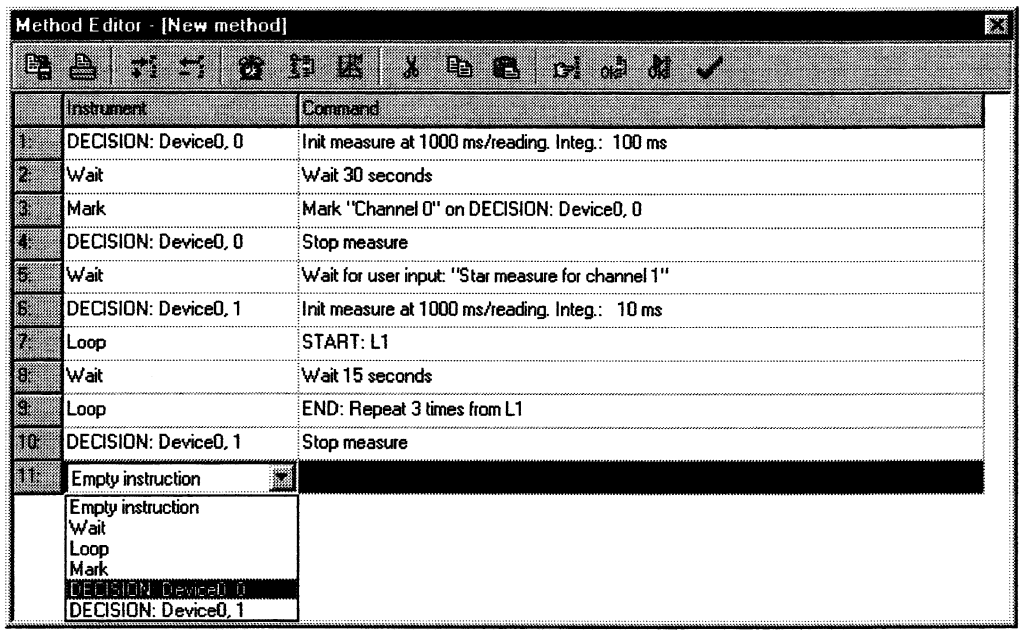

Fig. 9. Editor of the analytical methods of the AUTOANALYSIS program.

nate the use of the flexible tubing in peristaltic pumps, thus making the use of aggressive solvents or reagents more feasible.

Among the advantages of SIA in the first place it should be mentioned the fact that the manifold is more simple and universal than that of FIA. Thus, although in the latter technique the residence time in the reactors is fixed according to the tubing length, in SIA the manifold can remain fixed and control of the reaction times can be carried out by means of a computer internal timer. This device fixes the circulation of the liquids in the different directions, being able to stop the flows whatever time required. In SIA the use of peristaltic pumps can be completely eliminated, being replaced by glass syringes to which usually neither the samples nor the different reagents reach. In this way, SIA becomes a very robust technique from the point of view of the setting-up of monitoring systems of environmental parameters, since these systems do not tend to present a faulty calibration, they can easily manage aggressive reagents and/or solvents, which are at all times only in contact with glass or PTFE tubes. On the other hand, in FIA the peristaltic pump is usually permanently in movement, the analytical measurements -being or not carried out, giving rise to an inadequate reagent consumption, whereas in SIA the system only performs when measurements are required, thus, the reduction in consumption of both samples and reagents is drastic in relation to FIA. Thus, e.g. for a week in monitoring processes a consumption of ≈ 10 l of reagent per channel is required in FIA, whereas the former consumption is being reduced to 1.5 l in SIA. However, in spite of these advantages, SIA presents a series of disadvantages against FIA, the analysis frequency being the most important. FIA can be considered a technique in parallel, in which both the sample and the different reagents are simultaneously propelled by the peristaltic pump. However, SIA on its own account (and as stated by its name) operates by aspirating sample and reagents one after the other, which introduces two major critical aspects: a considerably decrease in the sampling rate (it is easily reduced to half as much in relation to FIA) and major difficulties in the mixture of sample and reagents.

Other of the inconvenients of SIA is the almost compulsory control of the whole system by incorporating a computer which imposes the performance of the instruction sequence in well defined periods of time in order to achieve a reproducible process. On the other hand, it is responsible for data acquisition and treatment (in FIA potentiometric recorders are more widely used, which allow the use of manual systems, although inconvenients in data treatment and storage are introduced). The hardly any presence up to present in the market of commercialized software of a general approach for SIA explains the fact that the development of the former technique has been considerable slower than that of FIA. Although being a major disadvantage, since setting-up of an automated SIA on one's own involves evident difficulties (there is no point in using manual SIA), however, it constitutes one of the advantages of SIA against FIA, especially when applying stop-flow techniques.

In spite of the above-mentioned disadvantages against FIA, SIA has finally presented a series of additional advantages initially not taken into account. Firstly, SIA has proved to possess an exceptional capacity in relation to previous sample handling, allowing to circulate the sample and reagents through several channels, to reverse flows, to handle aliquots, etc. On the other hand, SIA has proved to be a technique which can be designed to operate in a multiparametric way, which is of special interest when considering the design of environmental monitors. Usually, these monitors do not require a considerable sample frequency; at times carrying out measurements every 15 min or even at less frequencies is sufficient. Since the sample and the different reagents can be placed around the selection valve, the programming of the computer work for the determination of successive parameters which will characterise the sample quality becomes immediate. Thus, a monitor of waste water has been proposed with which the DQO, DBO, ammonium, nitrate, nitrite, total nitrogen, orthophosphate, total phosphorus, detergents, etc. can be sequentially determined every 15 min [29].

2.4. Multicommutation flow analysis (MCFA)

Multicommutation is a novel approach in flow analysis which can be implemented by using discrete commutation devices, such as three way solenoid valve. The approach has been used to perform binary sampling [30], making feasible the reduction of reagent consumption, sequential determinations [31,32] and sequential management of incompatible reagents in single line manifolds [32]. This technique has been proposed to significantly widen the determination ranges [33,34] (Fig. 4).

2.5. Multisyringe flow analysis (MSFA)

It is in fact a technique which is hereby described for the first time [35]. It has arisen with the aim to transfer the robustness of the SIA methods based on the use of syringes, to the FIA technique and, thus, solve the problem of using peristaltic pumps together with the inconveniencies related to flexible tubing which their use is based on. As shown in Fig. 5, in both MSFA and SIA, liquids are only in contact with the glass or PTFE tubing, which makes the use of aggressive reagents and solvents feasible. In order to make this technique competitive from an economic point of view against the remaining techniques, the first prototypes have been assembled adapting a typical burette of automatic tritations (like those used in SIA) to simultaneously enable the movement of four syringes, which can be of different capacity, allowing the different channels to perform at a different flow. In this technique the use of solenoid valves employed in the multicommutation techniques has been also incorporated to eliminate the critical aspects of the use of rotary motors. Thus, the problem of the detection of positions is solved and, besides, the rate in the selection of channels is increased.

The first prototype was constructed by incorporating only four syringes with their corresponding solenoid valves. In order to apply the system, this module should be used together with an injection valve. In the filling position of the burettes the injection valve is placed in the loading position and the samples aspirated by one of the syringes (W), whereas the remaining syringes aspirate the reagents which will be required in the analytical method. By commuting the valve in the injection position and using one of the syringes of the system to propel the sample (C) and using the remaining two to propel the reagents (R1 and R2), the device operates the same as FIA. However, the difference lies in the fact that reagent consumption is carried out only when a measurement is required, being independent from time and, therefore, being only dependent on the sampling frequency.

The incorporation of two additional commutation valves in the subsequent prototypes has increased the possibilities within the system, allowing to use the same module for the development of the multicommutation techniques. However, in this case flows are originated by liquid propelling and not by aspiration, thus reducing the risk from formation of undesirable bubbles.

On the other hand, the use of the two additional valves which operate replacing the injection valve is feasible (Fig. 6), thus, simplifying and decreasing the cost of the system even more.

2.6. Hyphenated techniques

The combination of the different flow techniques above mentioned is of great interest.

Thus, the advantages offered by the SIA technique can be of great use in relation to the previous sample handling, and subsequently, once the samples happen to be under appropriate conditions they can be injected following the criterion of other techniques. The determination of iron in water by carrying out its pre-concentration by SIA on a Chelex 100 column has been described [36]. The pre-concentrated iron is eluted with nitric acid, converging the eluate with another thiocianate flow according to the traditional FIA approach, to determine the red complex formed by spectrophotometric detection.

A simple combination which has led to excellent results is that of coupling the multisyringe technique to another normal burette (Fig. 7). The process is initiated by loading the sample as described in the corresponding MSFA section. Subsequently, the sample is injected and mixed with

other reagents, also as previously described. The additional syringe is used to end the passing of the remainder liquid through the detector, whereas, simultaneously the multisyringe starts a new cycle of reagent filling and sample loading, the analytical process being subsequently repeated. The extra syringe is filled with carrier when the multisyringe is performing the injection process. Thus, an alternative balance multisyringe-additional syringe takes place, which allows to achieve frequencies of up to 180 injections h^{-1}, with the robustness of MSFA, since no flexible tubes are used at any moment and the liquids are only in contact with glass or teflon.

Good results are also achieved by the coupling of SIA to MSFA, which has been applied to the determination of acidity in the lixiviates in the treatment of minerals [37].

Although this combination could be considered as a coupled technique, this terminology is applied when the flow technique is coupled to another different technique, such as gas chromatography, capillary electrophoresis [38] or mass spectrometry [39]. On same occasions the use of this terminology has been exaggerated, being extended to the cases in which the very expensive or sophisticated detectors have been used such as ICP. If the former inclusion was accepted almost all the proposed flow methods should be included within this group, since the connection the former flow system with one detection method or another takes place.

3. Software

One of the major difficulties which has retarded the development of the most modern flow techniques has been the availability of the programs which manage the system. As mentioned before one of the major advantages of FIA which has allowed an explosive development of publications is its feasibility in being assembled in the laboratory without requiring the use of a computer to control the system.

On the other hand, it is hardly unthinkable the application of the SIA, MCA and MSFA techniques together with their combined use without involving a computer, since residence times and other characteristics of the systems are directly controlled by computer. Until a few years ago software had to be developed by the users themselves, which explains the fact that the development of SIA, in spite of its advantages, has not been as spectacular as that of FIA. Likewise we believe that the generalization of MCA and MSFA techniques will be also delayed.

At present there are several commercialized programs or programs available for the SIA users, some of which have been already mentioned, cited by J.F. van Standen in a recent SIA review published in LRA [40], FlowTEK [41], DARRAY [42] and FIALab [43].

Frequently, one of the major limitations of these programs is the fact that they have been designed for excessively specific purposes and should be modified when requiring either the development of other applications or the change of the types of detectors. In order to avoid the former critical aspects, the program AUTOANALYSIS has been recently developed [44] to work under Windows of 32 bits. The design has been carry out to operate in four different layers, with their corresponding DLLs, being the first and fourth interconnected with the intermediate ones, however, at the same time the former layers remain isolated between them. This allows the developed analytical methods to be independent from the instrumentation used, being the incorporation of new instrumental modules feasible with only the development of the corresponding DLLs which will allow them to be controlled from the main module.

In Fig. 8 the menu of the AUTOANALYSIS program is shown. In the left window it can be noticed the communication channels opened for the connection of the different elements. In those to the right it can be observed how the HP-IB communication channel is selected (top window), to which a diode spectrophotometer is hung (bottom window).

Working at 32 bits implies a multiarea program making simultaneously feasible the application of developed flow methods, data treatment with the same program, document edition with other commercial programs, etc. The program has been

thought to work under the conception of laboratory unitary operations, with which the implementation of individual flow (FIA, SIA, MCA, MSFA) or coupled techniques (SIA-FIA, SIA-MSFA, etc.) is feasible. In Table 1 the different types of instruments and apparatus which can be controlled by the AUTOANALYSIS program and may be used for the configuration of automatic systems are specified.

In Fig. 9 the edition of an analysis method by the AUTOANALYSIS program is depicted.

4. Applications

Flow techniques have been widely used in the analysis of environmental parameters, and, especially, in water analysis, to which they are particularly adapted. In the E.Hansen [45] database, which may be accessed to by internet, more than 750 citations related to water analysis are found, most of which are based on the use of FIA. In the review of the former applications several types of waters, such as natural, residual, drinking, marine, estuary, salty, superficial, underground, refrigeration, energy co-generation waters, etc. are found.

4.1. Monitoring

Although many techniques have been developed to be used in the laboratory, being water a fluid easy to handle, one of the major possibilities of flow techniques is that of their application in the monitoring of parameters of interest, especially in on-line mode, which has given rise to several reviews [46–57] and even EPA regulations have been established [58,59].

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