ROLE OF FLOW INJECTION ANALYSIS IN ROBOTIC STATIONS

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ABSTRACT

Flow-injection (FI) manifolds incorporated to robotic stations are of great help in the development of analytical processes by shortening them. The robot develops steps of the process forbidden in FI (weighing, dissolution, etc.), and the hydrodynamic manifold performs in an expeditious way operations such as on-line separation, derivatization, transport to the detector, etc. Thus, a symbiotic effect is achieved in this hybridization, saving time and materials dramatically.

INTRODUCTION

Efficient automation of the preliminary operations in the analytical process is a challenge of today's analytical chemistry. In contrast to the other two steps of the analytical process (measuring and transducing of the analytical signal; data acquisition and processing) whose automation has reached a high level of development, preliminary operations have a series of drawbacks that hinder automation to be applied in a general way. The difficulties are derived from two aspects: the variety of sample aggregation states (solid, semi-solid, liquid and gas) and the number of operations that can be involved on the preliminary operations (e.g. sampling, sample amount measurement, grinding, sieving, homogenization, dissolution, destruction of organic matter, separation, analytical reaction, transport and introduction into the instrument, etc.). Despite these drawbacks, automation of these operations is mandatory as a way to eliminate or minimize the negative aspects involved in the manual development of these operations, such as slowness (preliminary operations can require 70-95% of the time of the overall analysis), errors due to human participation and last but not least, the risk for the user owing to the handling of toxic and dangerous reagents and solvents, which, finally, are released to the environment [1].

No doubt, there are brilliant approaches to solve the shortcomings involved in preliminary operations, such as the wide development of flow injection (FI) techniques, mainly for liquid samples, and the potential of robotic stations to automatize complex operations not able to reach by other automatized approaches. Nevertheless, none of the present options for automation in the panacea. Thus, the rapidity and simplicity of FI systems face the inability to automatize several operations (some of which are basic steps such as weighing). On the other hand, despite robots are the most powerful systems as a result of the great variety of processes they can develop, they have an inherent relative slowness compared to other systems, in addition to their high acquisition cost.

Figure 1 is an attempt to show the different degrees of difficulty involved in the introduction of samples of different aggregation state into an FI manifold: meanwhile a liquid sample can be directly inserted into the manifold, a solid sample requires one or several previous operations. Sometimes the pretreatment steps can be shortened by increasing the complexity of the hydrodynamic system [2].

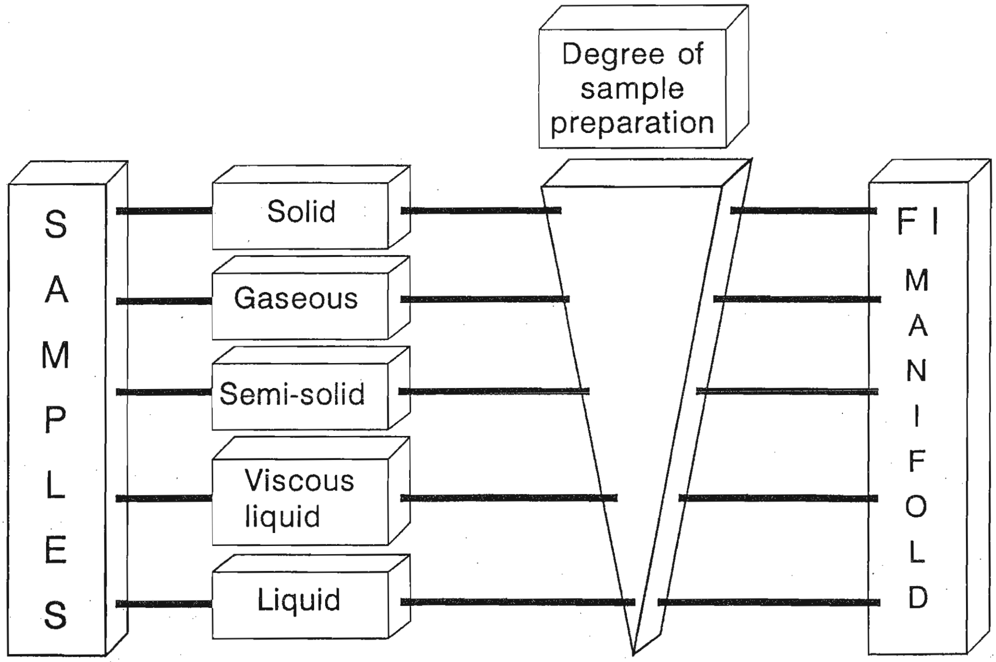

Figure 1. Gradation in the difficulty of sample manipulation in FI system depending on its aggegation state.

On the other hand, robotic stations can be very slow in performing simple operations such as the addition of a derivatizing forming colour reagent to a liquid sample and the monitoring of the colour developed, which are operations very easy to implement by an FI manifold.

These complementary features of FI systems and robotic stations can drive to a logical combined use, as a mean to exploit the advantages of both approaches also avoiding the respective limitations. Surprisingly this promising hybridization has been scarcely used so far. In fact, only three applications of this arrangement appear in the literature.

Two different approaches can be implemented in the robot-FI hybridization: A) A simple juxtaposition of automatic systems which work independently, the user acting as an active interface between both, or; B) An integrated system in which both subsystems work interrelated, thus eliminating human participation. In the first approach (Fig. 2A) the robot is devoted to automatize the complex, preliminary operations prohibited to FI systems, putting the partially treated samples in a rack, which is transported by the user to the FI system. This system acts as an automatic device for introducing the samples into the instrument, with ot without performing a prior separation and/or derivation step. In the integrated mode the FI manifold is a module of the robotic station devoted to introducing the sample into the detector (also with or without separation and/or reaction steps). In the latter there is not human participation involved (Fig. 2B), which is an evident advantage compared to the former approach. The robot/FI arrangements proposed so far are commented on.

A) ROBOT/FI OFF-LINE COUPLING

Two applications of the independent functioning mode of combining robotic stations and FI manifolds have been developed. The first application was the development of a method for the automatic analysis of used oils by ICP emission spectrometry [5]. The mission of the robot is to weigh the oil after heating the sample, add the volume of xylene necessary to achieve a 1+9 weight ratio and mix. The sample thus prepared fills a vial which fits in the FI analyzer's autosampler. Once the robot has finished this task, the vials are transported to the FI autosampler, which acts as a mere system for automatic introduction of the samples into the ICP spectrometer. The communication between both subsystems, that is, the transport of both samples and information generated in the robotic operations (dilution of each sample) is performed manually. The human participation is not totally eliminated in this approach, although the authors estimate that the automated system reduces manpower requeriments by two-thirds.

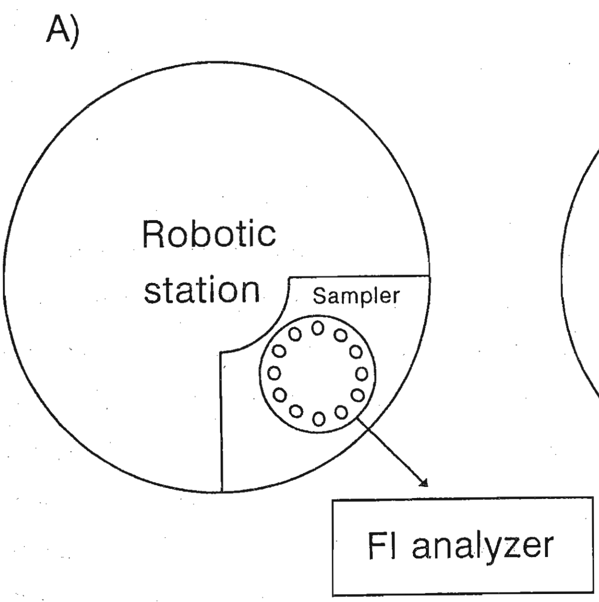

Figure 2. Alternatives to robot/FI arrangements. A) Off-line; B) integrated.

The second example is the automation of a method for the determination of total vitamin C in foods [6]. Here, the robotic station is used for performing the homogenization of the sample, weighing, addition of an extractant, centrifugation, filtration, and clean-up through a C_{18} column. After this treatment, the sample is manually transported to the FI autosampler. A derivatizing reaction is developed along the FI manifold to form a fluorescent product prior to introducing into the spectrofluorimeter. The authors do not comment how the information generated is transmitted between systems; presumibly this communication is also manual.

These two examples show two different ways to transmit information between off-line robot/FI arrangements: automatic treatment by means of an on-line microcomputer, or manual acquisition and treatment, former and latter examples, respectively.

B) INTEGRATED FI MANIFOLD/ROBOTIC STATION

When the FI configuration acts as a module of the robotic station the different operations involved in the overall process are distributed between modules searching for the highest efficiency of the overall system, but without human participation in the physical and logical communication between both subsystems.

There is a unique application of these integrated systems, which has been developed in the authors' laboratory, for the automation of the determination of total polyphenols in virgin olive oil [7]. The sequence of steps of the standard method is as follows: a) weighing of the oil, b) dilution with n-hexane, c) separation of the analytes by liquid-liquid extraction, d) derivatization of an aliquot of the extract with the Folin Ciocaltou reagent, e) filtration of the precipitate formed during the development of the colour and, f) measurement of the absorbance of the product. Apparently, this sequence gives little opportunity to FI systems owing to the complexity involved in each step. Introduction into the detector seems to be the single operation that the FI system could perform in an easy way, but the help would not be significant. Nevertheless, the task of the FI manifold can be much more effective if its job starts when the analytes have been isolated. Thus, the robot directly introduces the extract into the FI manifold, which performs the derivation reaction and the introduction into the detector (Fig. 3). In this way, the time required for the last step is dramatically shortened (1 min versus 1 h) and the filtration step is unnecessary as the precipitate does not appear in the short interval elapsed between injection and detection.

The border between the FI module and the robotic station is undefined in this approach as the robot, through its injection valve, introduces the extract from the test tube into the FI system, whose peristaltic pump is controlled by the robot. Moreover, the prior calibration of the FI system is performed by the robot, which prepares and injects different standard solutions from a stock solution of a standard polyphenol, and runs the calibration graph, which is later used for analyte quantification. The advantages of this hybridization are schematized in Fig. 4. The treatment of the information is performed by the controller of the robotic station, thus avoiding human participation totally.

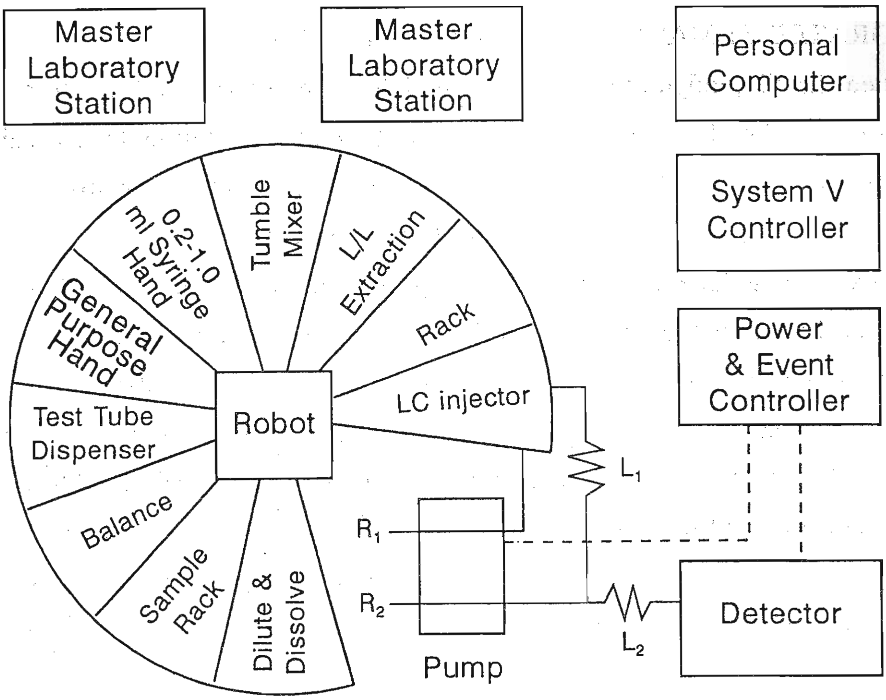

Figure 3. Robot/FI integrated approach for determination of total polyphenols in virgin olive oil.

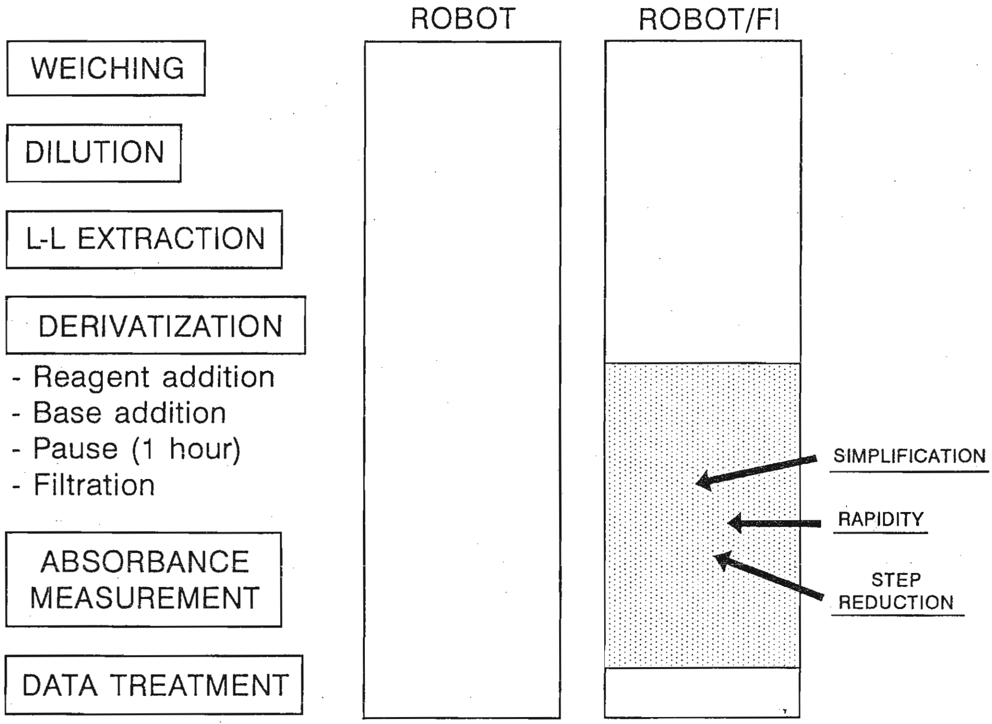

Figure 4. Simplification of the determination of total polyphenols in virgin olive oil by the integrated robot/FI approach.

FINAL REMARKS

Automation of the preliminary operations of the analytical process is a complex task which in general is not solved satisfactorily in a simple way. The combination of several automatic alternatives can result in a symbiosis with clear advantages compared with the separated use of the automatic systems. Following this phisolophy, the robot/FI hybridization appears as a promising approach since it allows to take advantage of the power and flexibility of the former and the rapidity and simplicity of the latter, as it has been shown in the applications developed so far.

A next step on this way could be the coupling of on-line continuous separation techniques to robot/FI arrangements, with a heavier charge on the FI subsystem which would result in a higher rapidity, simplicity and a lower cost of the overall automatic system for sample preparation.

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