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Review

A review on sequential injection methods for water analysis

Raquel B.R. Mesquita, António O.S.S. Rangel*

CBQF/Escola Superior de Biotecnologia, Universidade Católica Portuguesa, R. Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal

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ABSTRACT

The development of fast, automatic and less expensive methods of analysis has always been the main aim of flow methodologies. The search for new procedures that still maintain the reliability and accuracy of the reference procedures is an ever growing challenge. New requirements are continually added to analytical methodologies, such as lower consumption of samples and reagents, miniaturisation and portability of the equipment, computer interfaces for full decision systems and so on. Therefore, the development of flow methodologies meeting the extra requirements of water analysis is a challenging work.

Sequential injection analysis (SIA) presents a set of characteristics that make it highly suitable for water analysis. With sequential injection analysis, most routine determinations in waters can be performed more quickly with much lower reagent consumption when compared to reference procedures. Additionally, SIA can be a valuable tool for analyte speciation and multiparametric analysis. This paper critically reviews the overall work in this area.

Contents

1. Introduction

Water is an essential resource that is being threatened by pollution; therefore, the monitoring of water quality has become an issue of vital importance. The European Union has created the Water Framework Directive (WFD) in order to improve, protect and

* Corresponding author. Tel.: +351 225580064; fax: +351 225090351.
E-mail address: aorangel@esb.ucp.pt (A.O.S.S. Rangel).

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prevent further deterioration of water quality across Europe [1]. Accurate and frequent monitoring of water quality enables tighter control of the governmental regulations which is an important step in the reduction of the water pollution. It is estimated that, in European surface waters, the impact of pollution caused by industrial discharges of toxic substances has decreased 70% over the past 30 years [2]. This reduction has resulted from the implementation of stricter governmental regulations as much as the development of cleaner technologies.

The term "water" used in WFD includes most types of water, i.e. ground, surface and coastal waters. Several "water quality elements" are covered such as:

- Physicochemical properties – temperature, density, colour, turbidity, pH value, redox potential, conductivity, surface tension, suspended solids, total/dissolved organic carbon;
- Hydromorphological status – erosion and bench river characteristics;
- Biological – distribution and composition of the species and biological effects;
- Chemical monitoring – with particular emphasis on the contaminants in the list of priority pollutants.

Changes in water composition can be an indicator of pollution or contamination, so frequent water analysis is imperative. Some parameters are under strict regulation because of their risk to human health while others are not subject to enforceable regulation as they only cause visual or aesthetic effects [3]. More recently, the public concern for water safety has led to an increase on the use of disinfectants, which in turn has become a problem itself, if the carcinogenic by-products generated by the disinfectants are considered. Nevertheless, water disinfection is essential to ensure public health. Disinfectants prevent water contamination by bacteria but if in excess are harmful to human health, both directly and through by-products. In the last Analytical Chemistry biennial review on water analysis [4], the importance of disinfectants and their by-products as new contaminants was highlighted. These biennial reviews are focused on emerging contaminants and trends of analytical developments concerning water analysis.

The monitoring of water quality relies on effective routine water analysis, so this became a hot, sensitive and trendy issue. The range of methods, processes and tools available can be classified in different ways. A useful classification, revisited by Greenwood et al. [2], is based on the relationship between sample and analytical processes with three main categories: (i) *in situ*, (ii) on-line and (iii) off-line. Generally, the methods with no sampling, the methods with *in-situ* determination, use sensing devices such as probes inserted directly in the water body. Regarding on-line methods, the determination is carried out close to the water being monitored with direct feeding into the analytical system. In those cases, both discrete and continuous flow measurements can be performed.

Some major challenges in water quality monitoring include: a wide range of analyte concentration; variable salinity (wide range of ionic strength); colour or turbidity (mainly in waste waters); speciation; the need to mineralisation prior to quantifying the total amount. Analytes can be present in a high amount and so dilution may be necessary to fit the linear range, or they can be present in trace amounts and thus a preconcentration step is required. The variability in ionic strength may cause interferences in the chemistry itself or then influence the analytical signal, namely in spectrophotometric measurements. Water colour or turbidity may lead to high blank values which may adversely affect the limit of detection. The growing interest of environmental chemists in analyte speciation also poses an additional challenge, as some traditional methods only permit to quantify the total amount, namely when a reaction is used to quantify a certain analyte form may induce equilibrium shifts that unable to quantify the exact amount in that form. The interest of environmental chemists in analyte speciation relies on the tight relationship between speciation, bioavailability and toxicity. For example, aluminium is only bioaccumulated by organisms in the form of Al^{3+}. Organisms use nitrate as nitrogen source while the nitrite form is highly toxic. Furthermore, changes in the environment caused by pollution such as environmental acidification result in the release of the cationic form of several metals, their most bioavailable form. The impact to human health becomes a consequence of the environmental impact. With the sequential injection versatility, this issue of analyte speciation can be tackled.

On the other hand, there are situations in which the quantification of the total amount is required and so drastic digestion conditions must be created. All these issues increase the complexity of water analysis.

In addition, the analysis of water should also try to comply with the objectives of so-called Green Chemistry [5], in order to reduce and/or eliminate the use and generation of hazardous substances. In fact, an ironic situation is created when the analytical methodologies employed to monitor pollutants generate chemical wastes that are highly polluting themselves [5]. In some cases, the chemicals used in the analysis are even more toxic than the analyte itself, which makes the search of new alternatives even more pertinent.

In this scenario, flow systems may provide answer to the above mentioned challenges, as virtually every unit operation can be implemented in-line, and offer several advantages for routine analysis namely, high sampling rate, miniaturisation, low sample and reagent consumption. The variety and capability of flow techniques and flow equipment has increased significantly over the last three decades. Scale of the equipment has gone from bench size equipment, handling volumes measured in liters, to coin size equipment with volumes in the order of microliters. This review focuses on the sequential injection analysis (SIA) approaches that meet some of these challenges, choosing sequential injection analysis [6] among the different automatic flow techniques (flow injection [7], multicommuted flow injection [8], multisyringe flow injection [9], multipumping flow [10]). This choice was determined by the robustness of the equipment along with the compact size, the possibility of multiparametric determinations and the low reagent consumption. In addition, the easy coupling of external devices such as gas diffusion or dialysis units, resin packed columns and so on, enables the application to a wide variety of waters. These features result from the versatility of the sequential injection valve which enables a direct connection to the various reagents and/or to external devices.

2. Sequential injection analysis

2.1. Fundamentals

Sequential injection was proposed as an evolution to flow injection analysis, to overcome some of its perceived disadvantages, the requirement for a separate manifold for the determination of each parameter and the continuous consumption of reagents. Other flow techniques such as multicommutation, multisyringe and multipumping overcome the continuous consumption of reagents but maintain, in many circumstances, the requirement of physical reconfiguration for different methodologies. Sequential injection has the ability of performing different determinations without system reconfiguration (placing different reagents on the ports of the selection valve) and there can be a reagent saving associated to non-continuous consumption. In a SIA manifold (Fig. 1(I)), sample and reagent solutions are sequentially aspirated into a holding coil, being the aspirated volumes determined by the time and aspiration