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Review

Pulsed flows in flow analysis: Potentialities, limitations and applications

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ABSTRACT

In flow analysis, use of a steady and pulseless flow was considered essential for ensuring a reproducible handling of the flowing sample. To this end, peristaltic and syringe pumps have been the propelling device in the vast majority of the flow analysers. Recently, the number of applications involving pulsed flow has been increasing. Most of them refer to use of solenoid pumps, the essence of the so-called multi-pumping flow systems.

This review critically discusses the characteristics, potentialities and limitations of the pulsed flow systems, emphasizing the main advantageous characteristics of the streams involved, such as high radial mass transference and good mixing of the fluids. Diverse contributions ranging from instrumentation development to analytical applications are presented.

Contents

1. Introduction

Investigations on the influence of flow pattern[2] in analytical chemistry started at the first quarter of the last century. The need for fast solution mixing and in-line detection was increasing, and exploitation of flow-based strategies was the right answer to it [1]. Modifications in flow pattern influenced the mixing conditions, as highlighted in 1923 by Hartridge and Roughton [2], who reported vortex movements of fluids caused by Y-shaped and cylindrical mixing devices.

Mixing chambers were further used to improve the continuous monitoring required for repetitive assays. Convergent streams of sample, reagents and carrier solutions were generally established, and steady situations analogous to that of "sample infinite volume" [3] were approached. Flow-based analytical procedures were then

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[2] Flow pattern is herein used in a broad context, encompassing flow regime, flow rate and its temporal variations, as well as the characteristics of the flowing stream.

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developed mainly for clinical assays, and the determination of glucose in blood [4] and the evaluation of kinetic parameters in enzymatic reactions [5,6] can be selected as examples. Different strategies for modifying flow pattern were applied, and the addition of air bubbles played a relevant role in the context.

Air bubbles are inherent to segmented flow analysis [7]. In fact, their addition hinders sample intermingle, minimizes sample dispersion and scrubs the tubing inner walls. Stream segmentation was then considered a rule of thumb, as the established vortices inside every flowing segment were beneficial to improve the mixing conditions. Consequently, the segmented flow analyser underwent amazing development and is still worldwide used, especially in clinical chemistry and environmental management.

Nevertheless, air segmentation is not always essential, as demonstrated in flow-based applications relying on unsegmented streams, proposed after the inception of flow injection analysis [8,9]. Without segmentation, the entire analytical channel behaves as an uncompressible liquid column, allowing different approaches such as stream splitting, flow reversal, zone circulating, zone merging, zone trapping, zone stopping and zone sampling to be efficiently implemented [10]. For improving system versatility and efficiently controlling the analytical course, discrete computer-operated devices, such as the selecting valve of the sequential injection analyser [11] or the directional valves of the multicommuted flow analyser [12] have been exploited. Development led to the proposal of several modalities of flow analysis (*e.g.* multi-syringe flow injection, mono-segmented flow, flow-batch, multi-pumping flow, sequential injection, lab-on-valve, bead injection, stop-in-loop, all injection, and simultaneous injection-effective mixing analysis), all of them assigned by an acronym. As only minor differences are generally taken into account for specifying a given modality, this policy should be strongly discouraged. The theme was already presented in a jocose editorial [13].

Regarding fluid propelling devices, the peristaltic pump has been mostly used. It delivers an almost constant flow with a slight ripple effect due to action of the rollers. This effect is beneficial for reproducible additions of the air bubbles and confluent streams [14]. A too pronounced ripple characterizes the so-called pulsating flow. Syringe pumps have been also used, specifically in unsegmented flow systems [15], and the established laminar flow regime [16] leads to a pronounced sample broadening. Although beneficial in some applications, broadening may increase the sample dispersion, thus lessening sampling rate.

In order to minimize sample broadening, several strategies such as tubing coiling, use of specially designed reactors, manifold downsizing, etc. have been proposed. Modifications in flow pattern are also beneficial for minimizing this effect, and pulsed flows, originally applied to flow analysis in 1996 [17], play a relevant role in the context. As a typical laminar flow regime is not established, interaction of the involved solutions is improved. Development of this novel strategy for solution management led to the concept of pulsed flow chemistry [18].

Pulsed flows constitute themselves in the essence of multi-pumping flow analysis [19], which involves several discretely operated pumps strategically positioned in the manifold. This architecture is an additional feature towards enhanced system versatility. The pumps may perform different tasks such as driving solutions, improving mixing conditions, selecting sample and reagent aliquots, introducing these aliquots into the analytical path, establishing tandem streams, implementing fluidized beds, stopping the sample and/or providing commuting facilities. Multi-pumping flow analysis was already reviewed [20], yet a critical discussion on use of pulsed flows in flow analysis without restricting it to a specific system modality is missing. This is the goal of the present review, which emphasizes also the characteristics, potentialities, limitations and analytical applications of pulsed flow systems.

2. Pulsed flows

A literature survey reveals that the term “pulsed flow” has been indistinctly used for specifying both a stream of successive aliquots of miscible solutions flowing at a constant flow rate (Fig. 1a) and a stream of a single solution flowing at a pulsed manner (Fig. 1b). In the present review, the term “pulsed flow” is restricted to the latter situation: the stream moves at a very high flow rate during very short successive time intervals and remains stopped during relative long periods between pulses.

In this context, a pulsed flow is established by suddenly inserting fixed solution aliquots (pulses) at a given frequency. To this end, the solenoid pump is by far mostly used, yet piston, pressure pulse [18], piezoelectric and aquarium pumps have been scarcely used.

The solenoid pump, also referred to as membrane solenoid pump, consists of a solenoid-driven diaphragm and two unidirectional check valves located at the inlet and outlet for establishing the direction of the flow. Commercially available solenoid pumps are usually operated at 12 or 24 V under direct electric current. Manufacturers recommend application of nominal voltage pulses during a fixed time span (usually 0.1–0.2 s) followed by a period of inactivation. The recommended pulse span should not be exceeded in order to avoid overheating. On the other hand, it cannot be reduced at will for decreasing the delivered volume, as a precision drop may occur. The inactivation time is set for attaining the aimed averaged flow rate.

Advantages and limitations of the solenoid pumps are highlighted as follows:

- No pumping tubes are required. Chemical inertia is then inherent to the these pumps. Moreover, drawbacks related to lifetime, maintenance and slow variations in flow rates, often reported for peristaltic pumps, are minimized.
- Downsizing is inherent to the pump. This is an additional guarantee towards system miniaturization and portability.
- Energy requirement is minimal. This is a worthwhile aspect for analyses under field conditions.

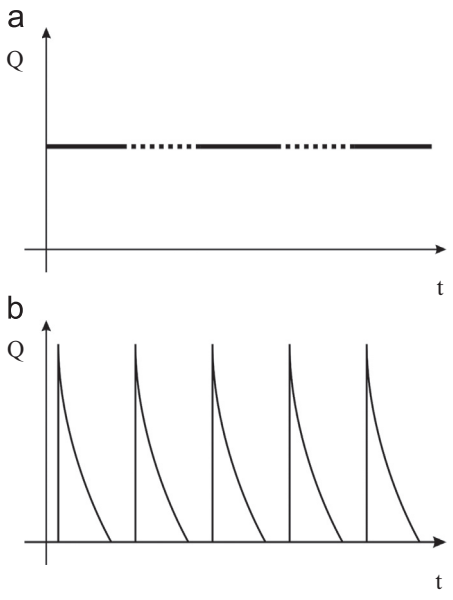

Fig. 1. Temporal variations in flow rates. Figure refers to successive aliquots of miscible solutions flowing at a constant flow rate (Fig. 1a) and to a single solution flowing at a pulsed manner (Fig. 1b). Q = flow rate; t = temporal coordinate; full and dotted lines = different involved solutions. Relaxation time too magnified for didactic purposes. See text for other details.