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Applications of flow techniques in seawater analysis: A review

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ABSTRACT

Flow analysis has been widely used in marine environmental monitoring applications due to its versatility, ruggedness, portability and excellent analytical figures of merit. Numerous scientific and technical literature and monographs have been published reporting the inclusion of different flow methods in standard analytical procedures. However, to the best of our knowledge, recently, there is no specific journal review that addresses the applications of flow techniques in seawater analysis (including estuarine, coastal and open ocean waters), which is more challenging for environmental analytical chemists. This paper summarizes the most relevant publications, from 2008 until the end of 2015, that refer to flow analysis of nutrients, metals, and carbonate system parameters, together with other related compounds in seawaters. It should be noted that, in order to be more specific to seawater analysis, this review excludes methods that are novel but have no application in saline samples, but especially includes those suitable for field or even *in situ* applications. Due to the rapid advances in flow analysis techniques in recent years and mounting global interest in marine environmental monitoring, this review is believed to be a relevant and timely resource for marine scientists, environmental chemists and analytical chemists.

Contents

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1. Introduction

Developed in 1957, Skeggs' truly ingenious concept of air-segmented continuous flow analysis (SFA or CFA) [1] resulted in the widespread use of continuous flow systems for performing discrete chemical analyses. Since then, there has been a continuous evolution of flow analysis systems. One of the most significant developments in this area is the flow injection analysis (FIA) technique, which was invented independently by Ruzika and Hansen [2] and Steart et al. [3] in the 1970s. FIA has been used for the development of excellent analytical methods because of its simplicity, feasibility, high sampling frequency, ease of automation, low consumption of reagents and samples, and elimination of contamination in closed environments. Sometimes, the term "flow injection analysis" is used synonymously with "flow analysis" or "automatic analysis". Various types of flow analysis techniques have been invented and developed in the past several decades. Some of the most relevant ones are: merging zone analysis [4], reverse flow injection analysis (rFIA) [5], sequential injection analysis (SIA, the second generation of FIA) [6], multi-commutated flow analysis [7], multi-syringe flow analysis (MSFA) [8], flow batch analysis [9], bead injection analysis [10], lab-on-valve (LOV, the third generation of FIA) [11], multi-pumps flow analysis (MPFA) [12], etc. Fig. 1 shows the commonly used manifolds for different kinds of flow analysis. Other detailed summaries of manifolds can also be found in previous literature [13,14].

The historical perspective on development of flow analysis is provided by several comprehensive review papers [15–20] and the introduction parts of some specific reviews [21–29]. Other information about the evolution of flow analysis and its innovative development can also be found from the websites (https://www.fia.unf.edu/ and http://www.flowinjectiontutorial.com/, where readers can find Dr. Hansen's continuously updated database about FIA, http://www.flowinjectiontutorial.com/Database.html), conferences (International Conference on Flow Analysis and International Conference on Flow Injection Analysis and Related Techniques [30]), and monographs [31–33 and previous monographs summarized by Ruzicka and Hansen in 2008 [19]].

Flow techniques have been widely used in water analysis [8,34–43] and have received considerable attention from marine environmental analytical chemists. However, to the best of our knowledge, recently, there is no journal review specifically addressing the applications of flow techniques in seawater analysis (including estuarine, coastal and open ocean waters). Recently, Šraj et al. [14] summarized the challenges in seawater analysis, including low analyte concentrations, variable salinity, complex matrix and ion interference (such as that from Ca^{2+} and Mg^{2+}), as well as the rigorous collection, storage and preservation requirements for these real samples. For example, for flow analysis with spectrophotometric detection, the changes in refractive index (e.g. salinity variation) between the sample and carrier can lead to two types of errors/anomalies. The first type involves the physical

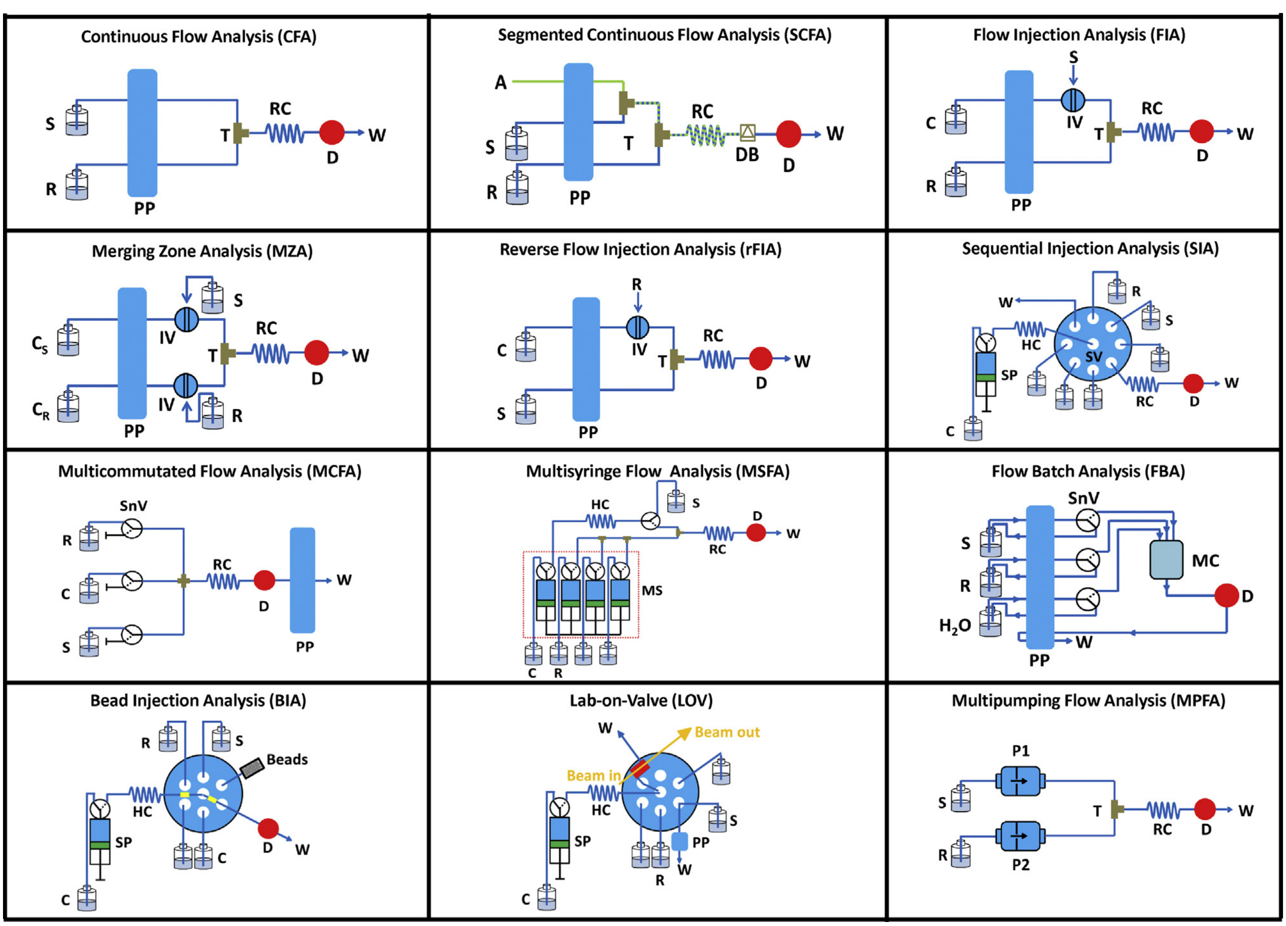

Fig. 1. Manifolds used in common flow analysis systems. S, sample; R, reagent; PP, peristaltic pump; T: tee; RC, reaction coil; D, detector; W, waste; A, air; DB, de-bubbler; C, carrier; IV, injection valve; C_S, carrier-sample; C_R, carrier-reagent; SP, syringe pump; HC, holding coil; SV, selection valve; SnV, solenoid valve; MS, multi-syringe; P1/2: pump1/2.