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A flow-batch analyzer with piston propulsion applied to automatic preparation of calibration solutions for Mn determination in mineral waters by ET AAS

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Abstract

The increasing development of miniaturized flow systems and the continuous monitoring of chemical processes require dramatically simplified and cheap flow schemes and instrumentation with large potential for miniaturization and consequent portability. For these purposes, the development of systems based on flow and batch technologies may be a good alternative. Flow-batch analyzers (FBA) have been successfully applied to implement analytical procedures, such as: titrations, sample pre-treatment, analyte addition and screening analysis. In spite of its favourable characteristics, the previously proposed FBA uses peristaltic pumps to propel the fluids and this kind of propulsion presents high cost and large dimension, making unfeasible its miniaturization and portability. To overcome these drawbacks, a low cost, robust, compact and non-propelled by peristaltic pump FBA is proposed. It makes use of a lab-made piston coupled to a mixing chamber and a step motor controlled by a microcomputer. The piston-propelled FBA (PFBA) was applied for automatic preparation of calibration solutions for manganese determination in mineral waters by electrothermal atomic-absorption spectrometry (ET AAS). Comparing the results obtained with two sets of calibration curves (five by manual and five by PFBA preparations), no significant statistical differences at a 95% confidence level were observed by applying the paired *t*-test. The standard deviation of manual and PFBA procedures were always smaller than 0.2 and 0.1 $\mu g\,L^{-1}$, respectively. By using PFBA it was possible to prepare about 80 calibration solutions per hour.

Keywords: Flow-batch analyzer; Automatic preparation of calibration solutions; ET AAS; Manganese; Mineral water analysis

1. Introduction

The minimization of human interaction in analytical procedures is an exhaustively persecuted target by the modern instrumental analytical chemistry studies, mainly when a large number of samples are involved [1,2]. In general, the automated procedures are independent of errors caused by the operator and provide high repeatability [3]. Several flow analyzers (FA) [4] have been developed in order to automate and to simplify analytical procedures [5–16]. However, even with the successful application of FA for automation and simplification of analytical methodologies, their flexibility and versatility are still limited. The FA manifolds require significant changes in their physical assemblies when it is necessary to analyze samples with a large variation of analyte concentration and/or physical–chemical properties.

Automated micro batch (AMBA) and flow-batch analyzers (FBA) proposed by Sweileh and Dasgupta [17,18] and Honorato et al. [19], respectively, are systems more flexible and versatile (multi-task characteristic). In these analyzers, it is possible to work in any analyte concentration range as well as to implement different analytical processes. It may be accomplished just by changing the operational parameters in their control software, without significant alterations on the physical configurations of the analyzer. AMBA and FBA combine favourable

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characteristics of both flow and batch analyzers (BA). As in FA, the transportation of reagents, samples or other solutions are carried out in a flow mode, and, as in BA, the sample processing is carried out into a mixing chamber (MC). In AMBA, an injecting loop is used on the sampling stage (as in FA), while in FBA the sample amounts are added into the MC by controlling the ON switching time of one solenoid valve.

As most of the FA, FBA and AMBA also present good precision and accuracy, high sample throughput and low contamination, consumption, manipulation of reagents and samples, cost per analysis and waste liberation for the environment, etc. They have been used to implement several analytical procedures such as: titrations [19,20], analyte addition [21,22], internal standard [23], screening analysis [24], exploitation of concentration gradients [25], on line matching of pH [26] and salinity [27], liquid–liquid extraction [17], distillation of volatile analyte [17], sample digestion [28] and kinetic approach [18].

In general, FBA and AMBA present the following characteristics: the use of solenoid valves and MC; highly precise fluid aliquots can be delivered by microcomputer controlling the ON valves switching times; high sensitivity because the physical and chemical equilibria inherent to the analytical processes may be attained and the dispersion and/or dilution of the samples may be negligible; the analytical signal measurements can be performed in flow cells or directly inside MC and the multicommutation [29,30] may be used in order to manipulate the fluids in a simultaneous and/or in an intermittent way.

In spite of their favourable characteristics, the previously proposed FBA and AMBA make use of a peristaltic pump and/or pneumatically pressurized reservoirs to propel the fluids. These kinds of propulsion result in manifolds with large dimensions, making their miniaturization and portability unfeasible. To overcome these drawbacks, a low cost, robust, compact flow-batch analyzer based on piston propulsion is proposed. This new approach to accomplish automatic analysis was designed to add a new study prospect in the present flow-batch technique. It was named as the piston propelled flow-batch analyzer (PFBA) because it uses a step motor-controlled piston coupled to the MC. To illustrate the feasibility of PFBA, it was applied to prepare calibration solutions for determination of manganese in mineral waters by electrothermal atomic absorption spectrometry (ET AAS). It is worth noting that the most critical and time-consuming steps of an analytical methodology, during which errors may be introduced, are the sample pre-treatment and the preparation of calibration solutions. The proposed system is a good alternative to perform these tasks.

2. Experimental

2.1. Reagents and solutions

The 1000 mg L^{-1} Mn stock solution was prepared from a Titrisol (Merck, Germany) ampoule in 0.5% (v/v) bidistilled HNO_3 (Merck, Germany). Calibration solutions were prepared by dilution of Mn stock solution in 0.5% (v/v) HNO_3. A 0.5% (v/v) bidistilled HNO_3 was used as the blank solution.

Table 1
Graphite furnace heating program of the Shimadzu AA6800 for determination of Mn in mineral water samples. The optimized pyrolisis and atomization temperatures were 2100 and 700 °C respectively

Step	Temperature (°C)	Time (s)		Gas flow rate (mL min^{-1})
		Ramp	Hold	
Drying 1	110	10	15	500
Drying 2	250	7	15	500
Pyrolysis 1	700	45	10	500
Pyrolysis 2	700	0	10	500
Atomization[a]	2100	0	5	0
Clean-out	2300	0	3	500

[a] The signal reading is performed in this step.

For the measurements of minimum times for switching ON valves, the dye solution was composed of 0.1 mol L^{-1} acetic acid/sodium acetate buffer, a 1000 mg L^{-1} Fe(II) in medium of 0.5 mol L^{-1} HCl prepared from a Titrisol (Merck, Germany) ampoule and the chromogenic reagent was a 0.25% (w/v) 1,10-phenantroline solution prepared in medium of 0.05 mol L^{-1} HCl.

All solutions were prepared with chemicals of analytical grade and freshly distilled-deionized water from a Millipore Milli-Q device. The mineral water samples were purchased in local supermarkets and analyzed without any previous treatment.

2.2. Instrumental parameters and operation of the spectrometer

A Shimadzu AA6800 furnished with a longitudinally heated graphite tube atomizer was used for all atomic absorption measurements and pyrolytic-coated graphite tubes were used. Samples were delivered to the furnace using a Shimadzu ASC-6100 auto sampler and stored in acid washed polypropylene cups prior to injection. The lamp used was a Mn hollow cathode lamp (Hamamatsu Photonics) operated at 10 mA; the wavelength at 279.5 nm was used with a slit-width of 0.2 nm. The inert gas used was argon (99.999%). Dilutions were carried out with calibrated Eppendorf pneumatic pipettes. The graphite furnace heating program is given in Table 1. The volumes taken of all solutions were always 20 μL.

2.3. The piston propelled flow-batch analyzer (PFBA)

The proposed analyzer is shown in Fig. 1a. Four Cole Parmer three-way solenoid valves were used: V_B and V_{CS} to direct the blank and work calibration solution or sample towards MC, respectively; $V_{D/S}$ to seal the MC outlet during the preparation of calibration solutions or to discharge these solutions or diluted samples of MC and $V_{A/W}$ to direct these solutions into the cup of the spectrometer auto sampler or towards waste.

A Pentium 550 MHz microcomputer was used to control PFBA, the spectrometer and to acquire and treat the analytical data. Software written in Labview® 5.1 with a friendly interface and easy operation was developed to manage PFBA. An electronic actuator (EA) was used to increase the power of the