A critical comparison of constant and pulsed flow systems exploiting gas diffusion

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A B S T R A C T

Considering the beneficial aspects arising from the implementation of pulsed flows in flow analysis, and the relevance of in-line gas diffusion as an analyte separation/concentration step, influence of flow pattern in flow systems with in-line gas diffusion was critically investigated. To this end, constant or pulsed flows delivered by syringe or solenoid pumps were exploited. For each flow pattern, two variants involving different interaction times of the donor with the acceptor streams were studied. In the first one, both the acceptor and donor streams were continuously flowing, whereas in the second one, the acceptor was stopped during the gas diffusion step. Four different volatile species (ammonia, ethanol, carbon dioxide and hydrogen sulfide) were selected as models. For the flow patterns and variants studied, the efficiencies of mass transport in the gas diffusion process were compared, and sensitivity, repeatability, sampling frequency and recorded peak shape were evaluated. Analysis of the results revealed that sensitivity is strongly dependent on the implemented variant, and that flow pattern is an important feature in flow systems with in-line gas diffusion.

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1. Introduction

Constant or pulsed flows have been generally exploited in flow analysis, and the related flow patterns may influence the performance of the analyzer. These flow patterns depend on the fluid propeller device, generally peristaltic or piston pumps for constant flows, or solenoid pumps for pulsed flows. Under constant flow, all fluid elements are displaced following parallel trajectories, and the pronounced radial gradient of the linear flow velocities leads to a parabolic profile of velocities inside the sample zone [1]. Consequently, laminar flow conditions are established. On the other hand, a pulsed flow is established by successive and sudden insertions of small solution aliquots, leading to a chaotic movement of the fluid elements. Turbulent mixing is then noted during the pulse insertions [2], and this aspect favors the radial mass transport and homogenization of solutions, thus improving the mixing conditions and reducing the sample dispersion. As the differences in linear speeds of the fluid lines are reduced, tailing effects are minimized.

Influence of flow pattern in flow analysis has been emphasized in different applications [3], and the superior performance of

pulsed flow systems has been demonstrated in relation to system portability [4], slow chemical reactions [5], heat transfer [6], solid phase extraction involving fluidized beds [7] and immobilized reagents [8]. In comparison with constant flow systems, pulsed flow systems are generally characterized by improved sensitivity, repeatability, analytical frequency, reduced sample and reagent consumptions and versatility.

Gas diffusion (GD) is a worldwide exploited analyte separation/concentration process and its implementation in flow analysis may overcome some drawbacks inherent to GD under batch wise conditions [9]. Several analytical procedures with in-line GD, relying on either constant or pulsed flows, have been recently reported [10], and the superior performance of pulsed flow systems in relation to constant flow systems was already stressed [11]. However, a systematic investigation of the influence of flow pattern in analytical systems with in-line GD was not yet carried out.

Selectivity and sensitivity are dependent on the physical characteristics of the donor and acceptor streams (*e.g.* flow rate, chemical composition, pressure, and flow direction), manifold design, reagent concentrations and GD-cell geometry (including type of semipermeable membrane) [12,13]. Moreover, variants involving acceptor and donor streams continuously flowing (AF), acceptor stream stopped and donor stream flowing during GD (AS), exploitation of stream segmentation and use of oscillating streams have been exploited [14,15,16]. With the AS variant, in-line

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concentration of the volatile species, thus sensitivity, is generally favored [14,17].

The aim of this work was then to critically compare the influence of flow pattern in flow systems exploiting in-line GD. To this end, a multi-syringe flow injection system and a multi-pumping flow system, involving constant or pulsed flows, were designed as similar as possible to each other, the only difference being the fluid propelling device, piston or solenoid pumps for delivering constant or pulsed flows, respectively. Ammonia, ethanol, carbon dioxide, hydrogen sulfide were selected as model volatile species, and the AF and AS variants were considered. System performance was evaluated under all the investigated situations, in terms of efficiency of mass transport during GD, repeatability, sampling frequency and recorded peak shape.

2. Experimental

2.1. Solutions

All solutions were prepared with analytical-grade chemicals from Scharlau SA (Barcelona, Spain) and deionized water (resistivity > 18.2 MΩ cm) provided by a Milli-Q system. The reagents and standard solutions are presented in Table 1.

2.2. Apparatus

A model Bu4S burette from Crison Instruments S.A. (Alella, Barcelona, Spain) equipped with four 5-mL glass syringes, model TLL SYR from Hamilton (Bonaduz, Switzerland), was used for establishing the constant flow inherent to the system in Fig. 1a. Each syringe head included a three-way solenoid valve accountable for directing the pumped solution towards either the manifold or the solution reservoir for refilling. An additional model STV-3 1/4UKG three-way solenoid valve from Takasago (Nagoya, Japan) was used for inserting the standard solutions. Its central port was connected to the ON port of the syringe head valve through a 2.2 mL holding coil (HC) and its ON and OFF ports were connected to the standard reservoir and to the manifold, respectively. This valve was controlled through an auxiliary supply port of the burette.

In the pulsed flow system (Fig. 1b), four model P/N 120SP1220-5TV solenoid pumps with 25-μL stroke volume from Bio-Chem Inc. (Boonton NJ, USA) were used as liquid drivers. For delivering 1.0 or 2.0 mL min^{-1} flow-rates, the pumps were actuated in a synchronized way at 0.67 or 1.33 Hz, respectively. The three-way valve was likewise accountable for introducing either the standard (ON) or the carrier (OFF) solutions. The solenoid pumps and valves were controlled by a multi-pumping module from Sciware System SL (Bunyola, Spain).

The RC$_1$ and RC$_2$ coiled reactors (length=100 cm, inner volume *ca* 0.5 mL), the holding coil and the transmission lines were made of PTFE (polytetrafluoroethylene) tubing (i.d.=0.8 mm), and the
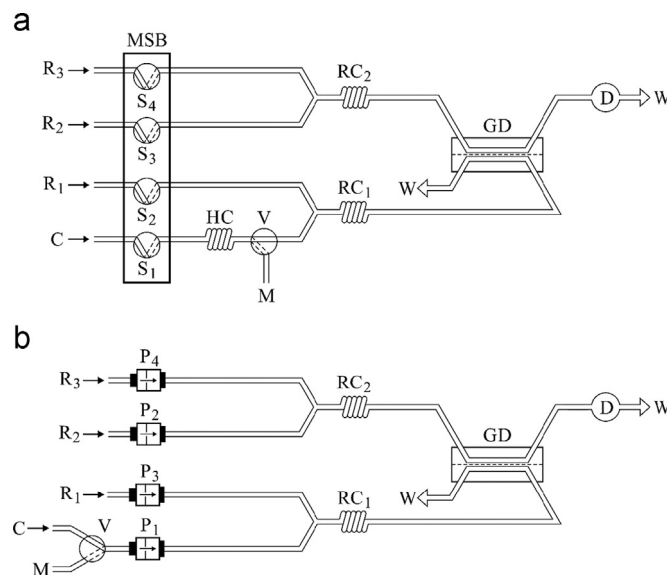

Fig. 1. Flow diagrams of the constant (a) and pulsed (b) flow systems. M=model species solution; Ri=reagents; C=carrier stream; MSB=multi-syringe burette with Si syringes; Pi=solenoid pumps; V=three-way solenoid valve; HC=holding coil; RCi=coiled rectors; GD=gas diffusion cell with the membrane specified by a traced line; reaction coil; D=flow-through detector; W=flask for waste collection. Two syringes (S$_1$, S$_3$) or pumps (P$_1$, P$_3$), three syringes (S$_1$, S$_2$, S$_3$) or pumps (P$_1$, P$_2$, P$_3$) and four syringes or pumps are need for EtOH, NH$_3$ or CO$_2$ and H$_2$S, respectively. For H$_2$S, the acceptor stream is formed by converging the R$_2$ and R$_3$ streams, and mixing them inside the RC$_2$ reactor. For details, see text.

connectors and GD-cell were made of PMMA (polymethylmethacrylate). PTFE tubes (length=30 cm, i.d.=1.5 mm) were used for aspirating the reagent and carrier solutions towards the pulsed flow system.

The GD-cell [17] was built-up by juxtaposing two identical rectangular PMMA blocks, each one with a U-shaped flow channel (width, depth, and length: 2.0, 0.7, and 128 mm). A Teflon® hydrophobic GD membrane from Lachat Instruments (Loveland CO, USA), recommended for ammonia GD by the manufacturer [18], was placed between the blocks, thus establishing separated donor and acceptor channels (inner volume=180 μL). The donor and acceptor streams flew though these channels in a countercurrent way.

Regarding conductometric detection, a lab-made flow cell [19] was connected to a model 525 conductometer from Crison Instruments S.A. The cell constant was calculated as 0.06 cm^{-1} by using a 0.01 mol L^{-1} KCl (1413 mS cm^{-1} at 25 °C) conductivity standard solution. Two scales (0.1–200 μS cm^{-1} and 0.01–20 mS cm^{-1}) were selected for NH$_3$ and CO$_2$ and their corresponding baselines were adjusted close to the maximum values in order to increase peak height. Measurements were done at every 0.2 s, and temperature correction was not applied because the laboratory temperature was stable enough [11].

Table 1
Composition of the involved solutions. Table refers to the flow systems in Fig. 1.

Stream	Model species			
	NH$_3$	CO$_2$	EtOH	H$_2$S
M	5.0–20.0 mg L^{-1} (as NH$_4$Cl)	2.0–10.0 mmol L^{-1} (as NaHCO$_3$)	10.0–60.0% (v/v)	5.0–25.0 mg L^{-1} S^{2-} (as Na$_2$S·9H$_2$O) in 25 mmol L^{-1} NaOH
C	Water	Water	Water	Water
R$_1$	25 mmol L^{-1} NaOH	25 mmol L^{-1} H$_2$SO$_4$	–	0.5 mol L^{-1} HCl
R$_2$	25 μmol L^{-1} HCl	10 mmol L^{-1} NaOH	0.3 mol L^{-1} K$_2$Cr$_2$O$_7$ in 4.0 mol L^{-1} H$_2$SO$_4$	5.0 mmol L^{-1} DMPD in 1.0 mol L^{-1} HCl
R$_3$	–	–	–	50 mmol L^{-1} Fe^{3+} (as FeCl$_3$·6H$_2$O) in 1.0 mol L^{-1} HCl