



## An expert flow system involving in-line prior assay for turbidimetric determination of chloride and sulphate in natural waters

Paula R. Fortes, Mário A. Feres, Elias A.G. Zagatto\*

Centre for Nuclear Energy in Agriculture, University of São Paulo, P.O. Box 96, Piracicaba 13400-970, Brazil

### ARTICLE INFO

#### Article history:

Received 16 October 2007

Received in revised form 11 March 2008

Accepted 17 March 2008

Available online 25 March 2008

#### Keywords:

Turbidimetry

Multi-pumping flow system

Prior assay

Expert system

### ABSTRACT

A multi-pumping flow system exploiting prior assay is proposed for sequential turbidimetric determination of sulphate and chloride in natural waters. Both methods are implemented in the same manifold that provides facilities for: in-line sample clean-up with a Bio-Rex 70 mini-column with fluidized beads; addition of low amounts of sulphate or chloride ions to the reaction medium for improving supersaturation; analyte precipitation with  $Ba^{2+}$  or  $Ag^+$ ; real-time decision on the need for next assay.

The sample is initially run for chloride determination, and the analytical signal is compared with a pre-set value. If higher, the sample is run again, now for sulphate determination. The strategy may lead to an increased sample throughput.

The proposed system is computer-controlled and presents enhanced figures of merit. About 10 samples are run per hour (about 60 measurements) and results are reproducible and unaffected by the presence of potential interfering ions at concentration levels usually found in natural waters. Accuracy was assessed against ion chromatography.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

In flow analysis, the result of an in-line performed prior assay can be taken into account for improving analytical strategies relying on real-time decisions [1]. The capacity of the analytical laboratory is then expanded, and the analytical results may become more reliable. As feedback mechanisms are involved [2], highly versatile flow systems are required. Multi-pumping flow systems (MPFS) [3] fulfil this requirement, as versatility is a core characteristic of them.

MPFS can be designed to behave as an expert system allowing, for instance, reduction in the number of assayed samples, simplification of the analytical procedure and/or lowering the reagent consumption.

The abilities of expert systems to perform a prior assay, interpret the gathered result and set conditions for further analytical course through concentration-oriented feedback mechanisms have been emphasised elsewhere [4]. Moreover, expert systems constitute themselves in a useful tool for screening analyses [5]. As a rule, the samples to be analysed are selected by

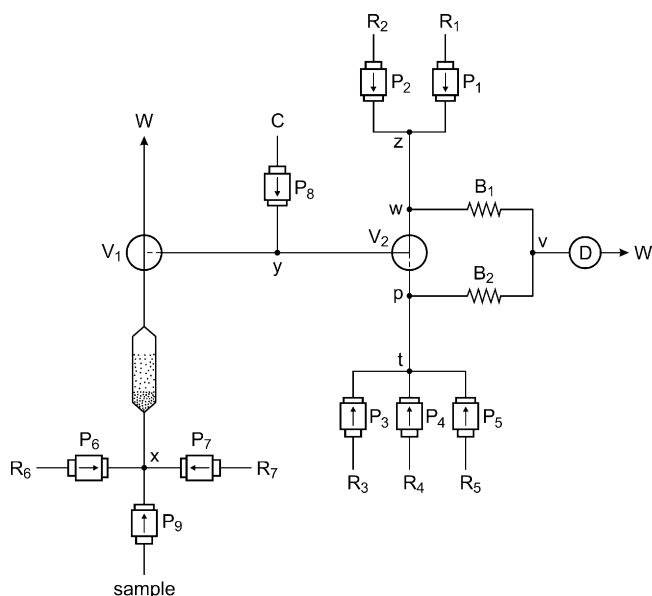
comparing the result of the prior assay with a pre-set value. The pre-set value is inherent to the focussed problem, and a binary answer such as yes/no, absent/present, low/high is always involved.

Regarding flow analysis, in-line screening may lead to a pronounced reduction in the total number of determinations, as demonstrated in the determination of zinc and phosphate in soil extracts [6]. A 30% lessening in the number of determinations was attained because determination of zinc was carried out only when phosphate was present in concentrations higher than a pre-set value. Recently, in-line selection of the detection technique allowed better results to be obtained in the sulphite determinations in untreated water samples [7].

The aim of the present work was to develop an expert MPFS for sequential turbidimetric determination of chloride and sulphate in surface waters, involving real-time decision for selecting the samples to be run for sulphate. Both methods are implemented in the same manifold, and the need for sulphate determination depends on the chloride concentration that is in-line estimated. In-line sample clean-up is performed by letting the sample to pass through a Bio-Rex 70 cation exchanger mini-column with fluidized beads [8]. Detection limits are improved by adding low amounts of sulphate or chloride ions to the reaction medium. In order to reduce uncertain-

\* Corresponding author.

E-mail address: [ezagatto@cena.usp.br](mailto:ezagatto@cena.usp.br) (E.A.G. Zagatto).



**Fig. 1.** Flow diagram.  $P_1$  = solenoid pumps;  $V_1$  = three-way valves;  $R_1$  reagent:  $0.01 \text{ mol L}^{-1} \text{ AgNO}_3$  in  $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $1.0 \text{ mL min}^{-1}$ ;  $R_2$  reagent:  $8.0 \text{ mg L}^{-1} \text{ NaCl}$ ,  $1.0 \text{ mL min}^{-1}$ ;  $R_3$  reagent:  $0.16 \text{ mol L}^{-1} \text{ Ba}$  in  $0.3\% \text{ (v/v) Tween-80}$ ,  $0.8 \text{ mL min}^{-1}$ ;  $R_4$  reagent:  $100 \text{ mg L}^{-1} \text{ SO}_4$  in  $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $0.8 \text{ mL min}^{-1}$ ;  $R_5$  reagent:  $0.3\% \text{ (w/v) EDTA}$  in  $0.2 \text{ mol L}^{-1} \text{ NaOH}$ ,  $0.8 \text{ mL min}^{-1}$ ;  $R_6$  reagent:  $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ,  $1.2 \text{ mL min}^{-1}$ ;  $R_7$ :  $1.5 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $7.5 \text{ mL min}^{-1}$ ;  $P_8$ : water;  $B_1$  and  $B_2$  = coiled reactors (75 and 250 cm); x, y, w, z, p, t, v: confluence points; D: detector (410/800 nm).

ties of the results, the number of analytical replications is in-line defined.

## 2. Experimental

### 2.1. Samples, standards, and reagents

All solutions were prepared with analytical-grade chemicals and deionised water.

Natural water samples were collected into polyethylene bottles, preserved with  $1.0 \text{ mL HNO}_3$  per litre, and filtered through a  $0.45\text{-}\mu\text{m}$  membrane cellulose filter [9].

The stock standard solutions ( $1000 \text{ mg L}^{-1} \text{ Cl}$  or  $\text{SO}_4$ ) were based on  $\text{NaCl}$  or  $(\text{NH}_4)_2\text{SO}_4$ . Working standard solutions were daily prepared in  $0.014 \text{ mol L}^{-1} \text{ HNO}_3$ , covering the  $0.0\text{--}20.0 \text{ mg L}^{-1}$  range.

The following solutions were used as  $R_1\text{--}R_7$  reagents (Fig. 1).  $R_1$ :  $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ AgNO}_3$  plus  $3.0 \text{ mol L}^{-1} \text{ HNO}_3$  (weekly prepared, stored in amber bottle);  $R_2$ :  $8.0 \text{ mg L}^{-1} \text{ Cl}$ ;  $R_3$ :  $0.15 \text{ mol L}^{-1} \text{ Ba}$  (as barium nitrate) plus  $0.3\% \text{ (v/v) Tween-80}$ ;  $R_4$ :  $100 \text{ mg L}^{-1} \text{ SO}_4^{2-}$  plus  $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ ;  $R_5$ :  $0.3\% \text{ (w/v) EDTA}$  (disodium salt) plus  $0.2 \text{ mol L}^{-1} \text{ NaOH}$ ;  $R_6$ :  $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ;  $R_7$ :  $1.5 \text{ mol L}^{-1} \text{ HNO}_3$ . Water was used as C carrier stream.

**Table 1**  
System operation

Step	Operation	Pump (Volume per pulse)	# Pulses	Valve position	
				$V_1$	$V_2$
1	Sampling	$P_1 (5 \mu\text{L}) + P_2 (5 \mu\text{L}) + P_8 (8 \mu\text{L}) + P_9 (8 \mu\text{L})$	100	1	1
2	Sample introduction	$P_1 (5 \mu\text{L}) + P_2 (5 \mu\text{L}) + P_9 (8 \mu\text{L})$	20	2	1
3	Reaction/column washing (phase 1)	$P_1 (5 \mu\text{L}) + P_2 (5 \mu\text{L}) + P_6 (8 \mu\text{L}) + P_8 (8 \mu\text{L})$	80	1	1
4	Reaction/column washing (phase 2)	$P_1 (5 \mu\text{L}) + P_2 (5 \mu\text{L}) + P_8 (8 \mu\text{L}) + P_7 (50 \mu\text{L})$	32	1	1
5	Sampling	$P_3 (5 \mu\text{L}) + P_4 (5 \mu\text{L}) + P_8 (8 \mu\text{L}) + P_9 (8 \mu\text{L})$	100	1	2
6	Sample introduction	$P_3 (5 \mu\text{L}) + P_4 (5 \mu\text{L}) + P_9 (8 \mu\text{L})$	60	2	2
7	Reaction/column washing (phase 1)	$P_3 (5 \mu\text{L}) + P_4 (5 \mu\text{L}) + P_6 (8 \mu\text{L}) + P_8 (8 \mu\text{L})$	80	1	2
8	Column and analytical path washing (phase 2)	$P_5 (5 \mu\text{L}) + P_7 (50 \mu\text{L}) + P_8 (8 \mu\text{L})$	32	1	2

Only  $P_i$  pumps specified below were switched ON; valve position 1 means the position specified in Fig. 1 and number 2 the alternative position.

The ion-exchange mini-column was prepared by packing the weakly acid cation exchanger Bio-Rex 70 (Bio-Rad, 50–100 mesh, sodium form) into a  $20\text{-mm long} \times 2.9\text{-mm i.d.}$  glass cylinder. In order to avoid resin losses during system operation, polyethylene foams were placed at both ends of the column. The resin was conditioned by passing a  $1.0\text{-mol L}^{-1} \text{ HNO}_3$  solution ( $1.0 \text{ mL min}^{-1}$ ) through it for about 10 min.

### 2.2. Apparatus

A FIALab-3000 flow analyser, including a model USB 2000 UV-vis Ocean Optics spectrophotometer furnished with an acrylic Z-shaped flow cell [10] (inner volume =  $10 \mu\text{L}$ , optical path =  $10 \text{ mm}$ ) was used. Wavelength was set as  $410 \text{ nm}$ .

The solenoid pumps (Bio-Chem Valve Inc., Boonton, NJ) with 5, 8 or  $50 \mu\text{L}$  stroke volumes and the MTV-3-N1/4UKG three-way solenoid valves (Takasago Electric Inc., Nagoya, Japan) were operated through a power driver based on the PCL-711 interface card (Advantech, Cincinnati, OH) and the Quick Basic 5.0 software.

Coiled reactors and transmission lines were build-up with polyethylene tubing (i.d. =  $0.8 \text{ mm}$ ) of the non-collapsible wall type.

### 2.3. Flow diagram

The proposed MPFS (Fig. 1) was operated according to the flowchart in Fig. 2, which emphasises the real-time decisions relying on previous measurements. Its operation is synthesized in Table 1.

The selected sample aliquot was initially handled according to the analytical procedure related to method A, here chloride. After threefold repetitive sample handling, the analytical results and uncertainties were estimated. If uncertainty was higher to an acceptable value (here 1%) the sample was run again (up to six replications). Thereafter, the averaged analytical result was compared with the pre-set threshold value. If higher, the sample was run again but aiming method B, here sulphate. If lower, next sample was run (method A).

The analytical cycle started by passing the sample through the ion-exchange mini-column with fluidized beads ( $P_9$  pump ON). Potential interfering cations that could co-precipitate with barium sulphate [11] and organic matter that could affect formation of the silver chloride turbidity [12] were then retained. The sample excess was directed towards waste.

For chloride determination, only  $P_1$ ,  $P_2$  and  $P_8$  pumps were switched ON. Thereafter,  $V_2$  valve rested in the position specified in Fig. 1 during a pre-set time interval that defined the sample aliquot in terms of pump stroke volume and number of pulses [3]. During sample insertion,  $P_8$  was switched OFF. After sample insertion,  $V_1$  was switched back to position in Fig. 1, and  $P_8$  was restored, thus pushing the sample selected aliquot through the analytical path related to chloride determination. At the w con-

Download English Version:

<https://daneshyari.com/en/article/1243105>

Download Persian Version:

<https://daneshyari.com/article/1243105>

[Daneshyari.com](https://daneshyari.com)