



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)

# A highly reproducible solenoid micropump system for the analysis of total inorganic carbon and ammonium using gas-diffusion with conductimetric detection

Camelia Henriques<sup>a</sup>, Burkhard Horstkotte<sup>a,b</sup>, Víctor Cerdà<sup>a,\*</sup>

<sup>a</sup> Laboratory of Environmental Analytical Chemistry, University of Balearic Island, CP: 07122 Palma de Mallorca, Spain

<sup>b</sup> Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Heyrovského 1203, CZ-50005 Hradec Králové, Czech Republic

## ARTICLE INFO

### Article history:

Received 30 May 2013

Received in revised form

30 September 2013

Accepted 3 October 2013

Available online 9 October 2013

### Keywords:

Multipumping flow system

Solenoid micropumps

Gas diffusion

Total inorganic carbon

Ammonium

Conductimetric detection

## ABSTRACT

In this work, a simple, economic, and miniaturized flow-based analyzer based on solenoid micropumps is presented. It was applied to determine two parameters of high environmental interest: ammonium and total inorganic carbon (TIC) in natural waters. The method is based on gas diffusion (GD) of CO<sub>2</sub> and NH<sub>3</sub> through a hydrophobic gas permeable membrane from an acidic or alkaline donor stream, respectively. The analytes are trapped in an acceptor solution, being slightly alkaline for CO<sub>2</sub> and slightly acidic for NH<sub>3</sub>. The analytes are quantified using a homemade stainless steel conductimetric cell. The proposed system required five solenoid micro-pumps, one for each reagent and sample. Two especially made air bubble traps were placed down-stream of the solenoid pumps, which provided the acceptor solutions, by this increasing the method's reproducibility. Values of RSD lower than 1% were obtained. Achieved limits of detection were 0.27 μmol L<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> and 50 μmol L<sup>-1</sup> for TIC. Add-recovery tests were used to prove the trueness of the method and recoveries of 99.5 ± 7.5% were obtained for both analytes. The proposed system proved to be adequate for monitoring purpose of TIC and NH<sub>4</sub><sup>+</sup> due to its high sample throughput and repeatability.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Ammonium and carbon dioxide are analytes of special interest in environmental monitoring since they are involved in nearly all biological processes, are transferable between all environmental compartments, such as atmosphere, hydrosphere, biosphere, and pedosphere. Their concentration levels in all compartments are influenced further by human activity. In natural waters, ammonium is an important nitrogen pool. It is the product of bacterial nitrogen fixation, decomposition of organically bound nitrogen, direct nitrogen elimination, and can easily be taken up by phytoplankton [1].

Anthropogenic emissions, especially originated from agriculture, industry, and urban waste contribute significantly to the global budget of atmospheric ammonia with estimation over 50% or 41 Tg of N per year [2]. This problematic has created the interest in effective NH<sub>3</sub> monitoring and analysis in different aqueous compartments including groundwater, surface water, and seawater.

Carbon dioxide is a key component of the carbon cycle [3] and is involved in the metabolism of all organisms [4]. It plays an important role in the occurrence of the photosynthesis and pH of

natural waters [5]. Increasing atmospheric CO<sub>2</sub> through human activity with about 24% over the last 50 years especially decrease the surface seawater pH (ocean acidification) and by this increases the solubility of carbonates, which affects the calcification process of mollusk's larvae [4]. For this reason, the development of methods for free CO<sub>2</sub> and total inorganic carbon (TIC) monitoring in natural waters and seawater is of pressing interest.

Gas diffusion (GD) is the separation technique "per excellence" for the determination of volatile species in complex matrix [6], while flow techniques (FT) such as flow injection analysis (FIA) [7], sequential injection analysis (SIA) [8], and multi-syringe flow injection analysis (MSFIA) [9] are the ideal tools to automate GD. Only by this combination, the construction of simple but yet reliable analyzer systems based on GD has become feasible achieving high selectivity, promising sensitivity, excellent precision, and rapidness [10–13].

Solenoid micro-pumps (SMP) are an economic alternative to the syringe and peristaltic pumps typically used for FIA, SIA, and MSFIA. A FT based on SMP has firstly been proposed and characterized Lapa et al. [14], denoted since then as multi-pumping flow systems (MPFS), although prior and successful use in FT has been reported [15].

SMP provide a semi-continuous flow with a highly pronounced pulsation causing intermediate turbulent conditions in the manifold. This improves the mixing efficiency compared to the former

\* Corresponding author. Tel.: +34 971 173 261; fax: +34 971 173 426.

E-mail addresses: [cameliahenriquez@gmail.com](mailto:cameliahenriquez@gmail.com) (C. Henriques), [burkhard.horstkotte@gmx.de](mailto:burkhard.horstkotte@gmx.de) (B. Horstkotte), [victor.cerda@uib.es](mailto:victor.cerda@uib.es) (V. Cerdà).

FT operating mainly in laminar flow conditions [16]. Moreover, SMP enable a high versatility and portability of the flow system due to their small size, independent operation, and their low energy consumption [12,17].

For the determination of  $\text{NH}_4^+$  using GD, the sample is injected into, or merged with, an alkaline solution and the formed  $\text{NH}_3$  diffuses across a gas-permeable membrane and is retained into an acidic acceptor solution. For the determination of TIC, the same principle is valid but the sample is mixed with acid and the formed  $\text{CO}_2$  is trapped into an alkaline acceptor solution. The trapped analytes are mostly determined by spectrophotometry [10,11,13,18], by potentiometry [19], or by conductometry [3,12,20–23]. Here, conductometry has some important advantages over the other detection techniques without loss of sensitivity. First, the required equipment, i.e. conductimeter and conductometric flow cell is simple, economic and can easily be miniaturized. Second, reagents and waste are diluted mineral acids and sub-milliliter amounts are required per analysis, so that the final method can be considered as environmentally friendly.

Combining the advantages of the MPFS as flow technique, GD as separation method, and conductometry as detection method, a further denoted C-GD-MPFS system has been developed and applied to the determination of both  $\text{NH}_4^+$  and TIC in different water samples.

This work was based on a previous one developed for the determination of ammonium with C-GD-MSFIA. Here, we intended to improve the former method in respect of rapidness, reproducibility, sensitivity, portability, and able to measure both ammonium and TIC in coastal waters. For these reasons, the MPFS technique was used instead of MSFIA.

## 2. Materials and methods

### 2.1. Reagents and solutions

All reagents and solutions were prepared with ultrapure Milli-Q water (Millipore SAS, Molsheim France). All reagents were purchased from Scharlau S.A. (Barcelona, Spain). A Teflon membrane provide by LCHAT (Loveland, USA) was used for GD [24].

For ammonium determination, the donor reagent was a mixture of sodium hydroxide ( $25 \text{ mmol L}^{-1}$ ) and sodium citrate dihydrate ( $200 \text{ mmol L}^{-1}$ ). A stock solution of  $0.01 \text{ mol L}^{-1}$  HCl

was prepared using hydrochloric acid 37% v/v. It was used to prepare the acceptor solution of  $25 \text{ } \mu\text{mol L}^{-1}$  HCl. A  $0.02 \text{ mol L}^{-1}$   $\text{NH}_4\text{Cl}$  stock solution was prepared by dissolving  $0.1070 \text{ g}$   $\text{NH}_4\text{Cl}$  in  $100 \text{ mL}$  of ultrapure water.

For TIC determination, concentrate sulfuric acid (reagent grade) was used to prepare a  $5 \text{ mmol L}^{-1}$  of  $\text{H}_2\text{SO}_4$  solution as donor reagent. A stock solution of  $1 \text{ mol L}^{-1}$  of NaOH was prepared by dissolving an appropriate amount of NaOH (reagent grade). It was used to prepare the acceptor solution,  $20.0 \text{ mmol L}^{-1}$ . A  $0.2996 \text{ mol L}^{-1}$  of  $\text{NaHCO}_3$  stock solution was prepared by dissolving  $2.516 \text{ g}$  of dried  $\text{NaHCO}_3$  in  $100 \text{ mL}$  of Milli-Q water.

All standard solutions were prepared daily by appropriated dilution of the respective stock solution with Milli-Q water. A commercial standard solution of  $0.1 \text{ mol L}^{-1}$  HCl from Scharlau SA. was used for total alkalinity determination by potentiometric titration of  $100 \text{ mL}$  of sample at room temperature [25].

### 2.2. Samples

Drinking water, coastal seawater, well water, and tap water samples were used to evaluate the proposed methods. They were measured directly and as soon as possible, without any further pretreatment such as filtration to avoid loss of analyte.

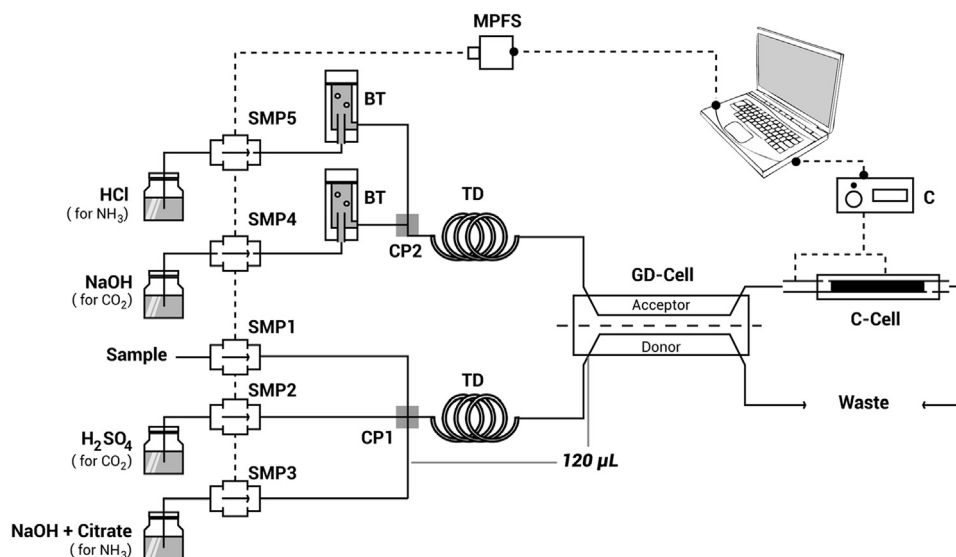
Four samples of coastal surface seawater (coastal water 1–4) from Palma Beach (Mallorca, Balearic Islands, Spain) were collected in dark glass bottles. They were hermetically sealed avoiding trapping of any air bubbles, and immediately refrigerated, transported to the lab, and measured.

Two different well water samples were collected in the same way than the seawater samples and likewise measured immediately. Two different commercial drinking waters with medium (Drinking water 1) and low (Drinking water 2) mineralization and a tap water sample were used further. The freshwater samples were only used to evaluate the determination method for TIC.

Samples were simultaneously measured with the proposed method for TIC determination and the potentiometric titration for total alkalinity quantification [25].

### 2.3. Instrumentation and manifold

The analyzer manifold is given in Fig. 1. All parts in liquid contact were of polymers resistant to the used chemicals, namely



**Fig. 1.** Manifold of used analyzer system for TIC and  $\text{NH}_4^+$  determination. Elements: SMP, Micropumping; MPFS, multipumping module; C, Conductimeter; C-Cell, Conductometric Cell (Tubino's electrodes); GD-Cell, Gas-Diffusion Cell; BT, bubble trap device; CP1, 4-way confluent point; CP2, 3-way confluent point; M, Membrane (LCHAT Instrument); TD, Tygon pulsation dampers; W: Waste.

Download English Version:

<https://daneshyari.com/en/article/1242106>

Download Persian Version:

<https://daneshyari.com/article/1242106>

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