

A Flow-Injection System with a Quartz Crystal Microbalance for the Determination of Dissolved Inorganic Carbon in Mineral Waters

Sandra Maria Oliveira Sá¹, Raquel P. Sartini², Claudio C. Oliveira², Elias A.G. Zagatto^{1,*}

¹Centro de Energia Nuclear na Agricultura, USP, Box 96, Piracicaba SP 13400-970, Brazil

²Centro de Ciências Agrárias, UFSCar, Araras SP, Brazil

Abstract

A flow-injection system with a quartz crystal microbalance was developed for the determination of dissolved inorganic carbon (DIC) in natural waters. A selected volume of sample is inserted into an unsegmented flowing stream, DIC in the established sample zone is converted to CO₂ by mixing with an acidic confluent stream, the gas diffuses through a PTFE gas-permeable membrane towards the acceptor stream, and monitoring is done by a quartz crystal microbalance. Effects of flow rates and composition of donor and acceptor streams, ionic strength, temperature, sample volume and potential interfering species were studied. The analytical curve was linear over the ranges from 0.5 to 20.0 mmol l⁻¹ DIC ($r = 0.9975$, $n = 8$) and the detection limit based on 3σ was estimated to be 0.15 mmol l⁻¹ DIC. Precise results (r.s.d. < 3 %, $n = 6$) were obtained at a sampling frequency of 48 h⁻¹. Accuracy was assessed against an official titrimetric method.

Keywords Dissolved inorganic carbon, flow analysis, quartz crystal microbalance, gas diffusion, mineral waters.

1. Introduction

As the chemical characterisation of carbon in environmental samples is of paramount relevance, it is important to monitor the concentration of inorganic carbon (IC) usually present as carbonate and bicarbonate in natural waters, sediments, soils, etc. IC is associated to the regulation of the buffering capacity of these media, and is generally determined as the difference between total and organic carbon. The official method for the determination of carbonate and bicarbonate involves a simple titrimetric procedure [1], but problems with endpoint visualisation and with evaluation of the titration data have been reported [2]. Alternatively, ion-chromatography [3], potentiometry [4], conductimetry [5] or spectrophotometry [5,6] has been exploited. In general, these techniques require a cumbersome prior step to convert the different carbon species to CO₂ (or another detectable species) usually involving wet sample digestion or sample combustion. As a consequence, the methods are time consuming, thus less suitable for *in situ* measurements.

Dissolved inorganic carbon (DIC) is an important fraction of the inorganic carbon in natural waters. So, there are several procedures for its determination, most of them carried out by continuous flow analysers, which are excellent tools for solution management [7]. In this context, the methods based on *in-line* CO₂ formation and monitoring by Fourier transform infrared spectroscopy [8] or by bulk acoustic wave impedance sensor (BAWIS) [9] should be highlighted. The latter method was designed for total inorganic carbon in natural waters and wastewaters. It involves the diffusion of CO₂ through a gas-permeable membrane from an acidic donor stream towards a buffered acceptor stream and the quantification of the trapped CO₂ by BAWIS.

The piezoelectric-based quartz crystal microbalance (QCM) can monitor very small variations in mass, density or viscosity of

the surrounding medium [10,11]. Its combination with flow-injection analysis is advantageous mainly for improving measurement precision and sample throughput. Moreover, separation/concentration steps, such as gas diffusion, are efficiently carried out. The above-mentioned features were already emphasised [12-15]. This paper describes the development of a flow-injection system with the QCM detector for the determination of DIC in mineral waters. The main innovation is that the *in-line* formed, diffused and collected CO₂ is monitored inside the aqueous medium, thus expanding the potentialities of the flow system.

2. Experimental

2.1. Samples, standards and reagents

The solutions were prepared with distilled-deionized water and analytical grade chemicals. Mineral water samples were obtained from a local supermarket. The stock standard solution, 200 mmol l⁻¹ DIC, was prepared by dissolving 4.201 g NaHCO₃ in 250 ml of water. The solution was standardised and kept in a refrigerator. Working standard solutions (0.0 – 20.0 mmol l⁻¹) were freshly prepared by suitable water dilutions of the above stock. The carrier stream (C in Fig. 1) was water, the conditioning stream (R₁) was a 0.25 mol l⁻¹ H₂SO₄ plus 1.0 mol KCl solution and the acceptor stream (R₂) was a 1.0 mmol l⁻¹ NaOH solution.

2.2. Apparatus

The flow diagram of the proposed system is shown in Fig. 1, which indicates the manually-operated sliding bar injector [7] in the sampling position. A model IPC-08 Ismatec peristaltic pump provided with colour-coded Tygon pumping tubes was used. The gas-diffusion unit (Fig. 2) comprised two straight channels

* Corresponding author
E-mail: ezagatto@cena.usp.br

(length = 70 mm, width = 1 mm, depth = 2 mm) engraved in Perspex blocks and separated by a planar PTFE gas-permeable membrane (1/2' x 260", TFEThread Seal Tape, USA). It was immersed in a thermostated water bath (0.5 °C precision). The manifold was made from 0.8-mm i.d. PTFE tubing and T-shaped Perspex connectors.

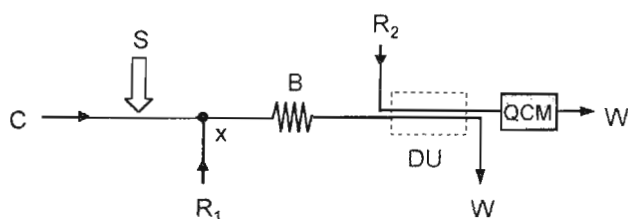


Fig. 1 Flow diagram. S = sample ($> 1 \text{ ml min}^{-1}$); L = sampling loop (10 cm, *ca* 50 μl); C = carrier stream (water, 0.8 ml min^{-1}); R_1 = conditioning reagent ($0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ in $1.0 \text{ mol l}^{-1} \text{ KCl}$, 0.4 ml min^{-1}); R_2 = acceptor stream ($1.0 \text{ mmol l}^{-1} \text{ NaOH}$, 1.2 ml min^{-1}); transmission line between injector and gas-diffusion unit = 17 cm; DU = gas diffusion unit inside a 30°C water-bath; QCM = quartz crystal microbalance; W = waste.

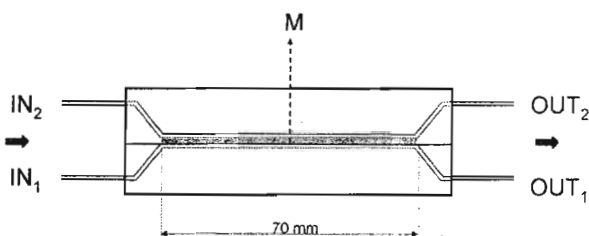


Fig. 2 The gas diffusion unit. Drawing to scale. The two perspex pieces, with the membrane (M) in-between, are held together by means of screws. IN and OUT = inlet and outlet for donor (1) and acceptor (2) streams; arrows = flow direction.

The QCM detector was a controlled-gain crystal oscillator driver actuating on a disc-shaped piezoelectric quartz crystal with gold-coated faces (crystal thickness *ca* 200 nm; effective area = 0.28 cm^2) [16]. The crystal electrode surface oscillated at a resonance frequency of 6.0 MHz, in a shear mode (AT cut), producing a strongly damped sinusoidal wave that propagated a distance λ into the electrolyte solution inside the flow-through cell (*ca* 20 μl). A single contacting face with the flowing electrolyte was then established. The oscillator was supplied with 5V by a dc power supply, and the oscillating frequency was monitored by a model 5384A Hewlett Packard frequency counter. Changes in the physical properties of the liquid up to a depth λ from the crystal surface are correlated with changes in the resonance frequency by the Kanazawa equation [17] and a microcomputer was used for data acquisition.

2.3. Procedure

The sample was aspirated to fill the sampling loop and manual switching of the injector to the alternative position intercalated the sample selected aliquot into the carrier stream. The established sample plug underwent dispersion while being pushed forwards, and an acidic stream was mixed at confluence point x in order to convert the analyte to CO_2 . Thereafter, the sample zone reached the diffusion unit and the CO_2 diffused through the semi-permeable membrane towards the acceptor stream, yielding a secondary sample zone. Passage of this zone (with the trapped CO_2) through the detector resulted in a transient variation in the monitored frequency that was

proportional to the analyte concentration in the injected solution. This variation was recorded as a peak and its height constituted the measurement basis.

The main parameters involved were investigated by injecting in triplicate the $0.0 - 20.0 \text{ mmol l}^{-1}$ DIC solutions into the system in Fig. 1. Influence of sample volume and reaction coil length were investigated within 50-250 μl and 10-100 cm, whereas flow rates were investigated by testing the various combinations specified in Table 1. Different acidic ($0.1 - 2.0 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, HCl or HNO_3) and alkaline (10 mmol l^{-1} tris(hydroxymethylamino)-methane, pH = 9.3, 1.0 mmol l^{-1} KOH in $0.0 - 1.0\% \text{ v/v}$ ethanol or 1.0 mmol l^{-1} NaOH) solutions were tested as donor and acceptor streams, respectively. Influence of temperature was investigated within 10 and 50°C by selecting different values for the temperature of the water bath into which the diffusion unit and the bottles with C and R_1 solutions were immersed. Moreover, influence of the ionic strength was investigated by adding $0.0 - 1.0 \text{ mmol l}^{-1}$ KCl to reagent R_1 .

After system dimensioning, the main analytical figures of merit were evaluated. Accuracy was assessed by running samples already run by the AOAC official method [1]. All analyses were undertaken on the same day.

3. Results and discussion

3.1. System design

Increasing the sample volume or reducing the coil length resulted in a pronounced improvement in sensitivity. The effect is due to the more efficient mass transfer of CO_2 through the membrane. In fact, the CO_2 formation is very fast and chemical equilibrium was attained even with very short analytical paths, as demonstrated in parallel experiments involving peristaltic pump stopping [18]. In addition, the QCM measurements were also quantitative. The sample volume and length of the analytical path, however, could not be modified at will in view of the compromise with sample throughput. With a sample injected volume of 50 μl and a 17-cm coil, reproducible measurements (r.s.d. usually $< 3\%$) were obtained and the dispersion coefficient [18] was estimated as 1.25.

Regarding CO_2 diffusion, it was observed that mass transport through the membrane was increased under lower flow rates (Table 1). The results suggest that slow flow rates provide a more efficient DIC transfer due to the increased residence time. Sampling rate, however, has to be reduced. For example, when the flow rates of donor and acceptor streams were equal with each other, and the flow rate was lessened from 1.2 to 0.4 ml min^{-1} , a pronounced enhancement in intensity of the analytical signal was noted, but the sampling frequency dropped from 48 and 20 h^{-1} , respectively.

The flow rate ratio of donor/acceptor streams demonstrated to be also a relevant parameter in system design. It was observed that for faster donor stream, sensitivity was improved because the same segment of the acceptor stream collected a higher amount of CO_2 . On the other hand, improved peak heights characterised by a short washing times were recorded when the flow rate ratio of the donor/acceptor streams was too high. In this situation, high sample dispersion was involved. The total flow rate, dictated by the rotation speed of the pump, was also a critical parameter. Thus, 1.2 ml min^{-1} was selected for both donor and acceptor streams. In this way, sensitivity was suitable and 48 samples could be run per hour.

Regarding pH and composition of the donor stream, experiments undertaken to investigate the conversion efficiency of HCO_3^- and CO_3^{2-} to CO_2 revealed the recorded signal

Table 1 Influence of flow rates. Resonant frequencies, in Hz, associated with the different time intervals elapsed after sample injection; DIC concentration = 1.0 mmol l⁻¹; T = 22 °C; q_A and q_D = total flow rate of acceptor and donor streams, in ml min⁻¹. Conditions: A: q_A = q_D = 0.4; B: q_A = q_D = 0.8; C: q_A = q_D = 1.2; D: q_A = 0.4 and q_D = 0.4; E: q_A = 0.4 and q_D = 0.8; F: q_A = 0.4 and q_D = 1.2; G: q_A = 0.4 and q_D = 0.4; H: q_A = 0.8 and q_D = 0.4; I: q_A = 1.2 and q_D = 0.4.

Time (s)	q _A = q _D			q _A ≤ q _D			q _A ≥ q _D		
	A	B	C	D	E	F	G	H	I
30	-1.0	-4.4	-7.1	-2.3	-3.4	-3.3	-0.6	-1.4	-1.5
40	-1.7	-7.3	-9.8	-3.5	-5.0	-7.5	-1.4	-2.7	-2.9
60	-4.0	-12.4	-4.3	-5.2	-9.2	-18.4	-3.4	-5.2	-5.5
75	-8.5	-10.1	0	-7.5	-14.8	-9.9	-7.0	-9.5	-7.9
90	-13.5	-5.7		-11.3	-19.8	-4.7	-12.4	-13.3	-8.9
105	-19.8	-1.9		-18.3	-14.6	-1.5	-18.2	-12.8	-7.9
120	-19.4	0		-22.2	-8.5	0	-19.0	-10.1	-5.4
150	-5.7			-7.2	-1.2		-11.3	-3.2	0
165	-1.8			-2.3	0		-5.0	0	
180	0			0			0		

increased by decreasing the pH of the donor stream until pH = 3, region where the analytical signal was almost constant. This result is in agreement with previous work [19]. The action of the three investigated acids was similar in relation to the CO₂ yielding, and sulfuric acid was elected in view of its low volatility. A concentration of 0.5 mol l⁻¹ was enough to obtain a sensitive (Fig. 3) and reproducible signal.

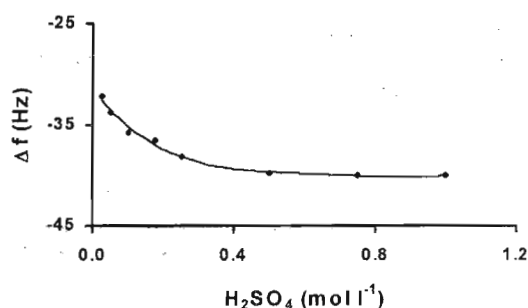


Fig. 3 Influence of acidity of the donor stream. Figure refers to 1.0 mmol l⁻¹ DIC and a water-bath temperature of 22 °C. Other conditions are the same as in Fig. 1.

The composition of the acceptor stream was a parameter playing a minor role in the system design. When 1.0 mmol l⁻¹ NaOH or KOH was used, almost the same increase in the resonant frequency inherent to baseline was noted (Fig. 4). This frequency increase reflects the difference in the sample environment equivalent to that between OH⁻ and CO₃²⁻, the loss of OH⁻ and the difference of mass between CO₃²⁻ and OH⁻. Addition of 10 mmol l⁻¹ tris(hydroxymethylamino)methane to the acceptor decreased the resonant frequency of the quartz crystal in relation to the baseline, and the corresponding analytical signal was about 25% lower in relation to use of NaOH or KOH.

The presence of ethanol in the acceptor stream has been recommended and was tested, but addition of 0.01 and 1.0 % v/v ethanol to the 1.0 mmol l⁻¹ NaOH (or KOH) led to sensitivity reductions of about 5 and 15 %, respectively. It should be emphasised that use of higher ethanol contents deteriorated the membrane. A white opacity was observed in the membrane and its ability to permit CO₂ diffusion was continuously lessened. Therefore, 1.0 mmol l⁻¹ NaOH was elected for use as the acceptor stream.

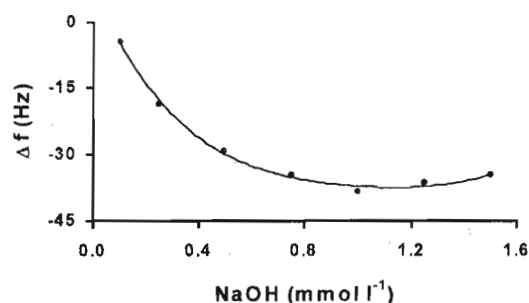


Fig. 4 Influence of alkalinity of the acceptor stream. Figure refers to 1.0 mmol l⁻¹ DIC and a water-bath temperature of 22 °C. Other conditions are the same as in Fig. 1.

Temperature manifested itself as a very important parameter and a linear relationship between temperature and sensitivity was noted (Fig. 5). Increasing the temperature of the thermostatic water bath from e.g. 20 to 30 °C increased the variation in resonant frequency, Δf, in about 60 %. Temperature beyond 30 °C favours the liberation of air bubbles and is therefore not recommended. The determination of DIC in water samples was then carried out at 30 °C.

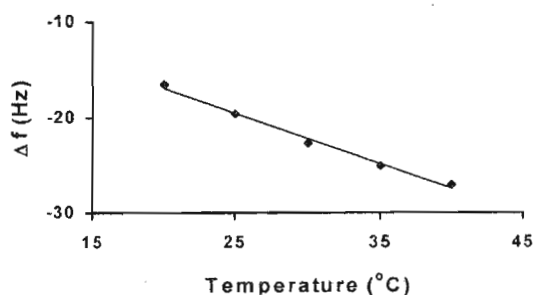


Fig. 5 Influence of temperature. Data correspond to temperatures of the water-bath into which some components of the manifold are immersed. For details, see text.

3.2. Figures of merit

PTFE membranes are effective barriers for ionic species [9] and have been exploited to improve selectivity in flow-injection procedures involving gas diffusion. With an acidic donor stream, the interference from volatile amines is negligible. In order to study the selectivity of the membrane separation, interferences from some volatile acids, which can diffuse through the membrane and affect the analytical signal, were investigated: results are presented in Table 2. The interferences would be significant only if SO₂ and CO₂ were present at the same concentration, and the HF and HCOOH contents should be at least twice the CO₂ concentration. A more severe interference was observed in relation to H₂S. When its concentration was higher than 20 % of CO₂, the accuracy was poor. Despite this, it is very unlikely that these interferents are present in such high concentrations in the assayed samples.

Table 2 Selectivity data. T = 22 °C. Other conditions are the same as in Fig. 1.

Interferant	Interferant (mmol l ⁻¹)	CO ₂ (mmol l ⁻¹)	
		Added	Measured
H ₂ S	0.4	2.0	2.16
SO ₂	2.0	2.0	2.50
HF	4.0	2.0	2.10
HCOOH	4.0	2.0	2.38

Moreover, addition of 1.0 mmol l⁻¹ KCl was investigated, leading to the conclusion that this reagent should be used to adjust the ionic strength thus avoiding the potential interference of chloride ions.

The proposed method was applied to the determination of DIC in mineral water samples and a throughput of 48 samples h⁻¹ was obtained, meaning a consumption of 37 mg H₂SO₄ and 60 µg NaOH per determination. The analytical curve exhibits linearity within the 0.5 - 20 mmol l⁻¹ DIC range and the regression coefficient was estimated as > 0.997. A typical equation of the analytical curve is:

$$y = -3.7775x - 7.4227, n = 8$$

where y = height of the recorded peak (maximum frequency variation, in Hz); x = DIC concentration in mmol l⁻¹.

Application of this system to the analysis of mineral waters resulted in precise results (r.s.d. < 3 %, n = 6) in agreement with those obtained with the reference method (Table 3).

Table 3 Comparative results. Data in mmol⁻¹ DIC.

Sample	Proposed method	AOAC method
1	2.28 ± 0.16	2.45 ± 0.71
2	1.57 ± 0.35	1.65 ± 0.55
3	2.31 ± 0.88	2.10 ± 1.03
4	5.73 ± 1.05	5.90 ± 1.54
5	2.35 ± 0.71	2.29 ± 0.94
6	2.85 ± 0.91	2.89 ± 1.45
7	1.79 ± 0.50	1.70 ± 0.86
8	1.89 ± 0.66	1.84 ± 1.13

4. Conclusions

The proposed system is simple, rugged and stable, thus highly recommended for the rapid determination of dissolved inorganic carbon (DIC) in mineral waters. The noise level of the detector is within ± 1 Hz, with a baseline drift of < 2 Hz per hour. The proposed procedure presents other favourable characteristics such as the requirement of simple and inexpensive equipment, the improved selectivity, and the use of very low reagent volumes. This latter feature meets the present tendency towards a clean chemistry. As the analyte is monitored in a liquid medium, the potentialities of the system are expanded, as the both the depleted sample zone and the collected gaseous species are available to be analysed for other chemical species. Therefore, the proposed method is promising for the analysis of other types of samples, including those with more complex matrices.

Acknowledgements

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