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Journal of Chromatography A, 1118 (2006) 56–61
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of total dissolved inorganic carbon in freshwaters by reagent-free ion chromatography

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Abstract

Studies of inorganic carbon cycle in natural waters provide important information on the biological productivity and buffer capacity. Determination of total inorganic carbon, alkalinity and dissolved carbon dioxide gives an indication of the balance between photosynthesis and respiration by biota, both within the water column and sediments, and carbon dioxide transfers from the water column to the atmosphere. There are few methods to measure and distinguish the different forms of inorganic carbon, but all require a measure or an indirect quantification of total inorganic carbon. A direct measurement of TIC in water is made possible by the introduction of electrolytic generated hydroxide eluent in ion chromatography which allows to detect a chromatographic peak for carbonate. The advantage of this method is that all the inorganic forms of carbon are converted in carbonate at eluent pH and can be detected as a single peak by conductivity detection. Repeatability of carbonate peak was evaluated at different levels from 0.02 to 6 mequiv. l^{-1} both in high purity water and in real samples and ranged from 1 to 9%. The calibration curve was not linear and has to be fitted by a quadratic curve. Limit of detection was estimated to be 0.02 mequiv. l^{-1}. Accuracy has been estimated by comparing ion chromatography method with total inorganic carbon calculated from alkalinity and pH. The correlation between the two methods was good ($R^2 = 0.978$, $n = 141$). The IC method has been applied to different typologies of surface waters (alpine and subalpine lakes and rivers) characterised by different chemical characteristics (alkalinity from 0.05 to 2 mequiv. l^{-1} and pH from 6.7 to 8.5) and low total organic carbon concentrations. This analytical method allowed to describe the distribution of TIC along the water column of two Italian deep lakes.

Keywords: Ion chromatography; Total inorganic carbon; Freshwaters

1. Introduction

Studies of inorganic carbon cycle in natural waters provide an important indicator of their biological productivity and buffer capacity. Determination of total dissolved inorganic carbon (TIC), total alkalinity (Talk) and dissolved carbon dioxide gives an indication of the balance between photosynthesis and respiration by biota, both within the water column and sediments, and carbon dioxide transfers from the water column to the atmosphere [1,2]. Research on carbon dynamics indicates that oceans and terrestrial areas are generally sink for carbon dioxide [3]. However it is not clear whether freshwater bodies release or take up carbon dioxide [4]. On the consequence there is a huge interest in developing reliable analytical methods for the accurate determination of inorganic carbon species.

By knowing the concentrations of TIC and pH, it is possible to estimate the equilibrium concentrations in water of all inorganic carbon forms, according to the following equations:

$$\mathrm{H_2CO_3}^* = \mathrm{TIC}\alpha0$$

$$\mathrm{HCO_3}^- = \mathrm{TIC}\alpha1$$

$$\mathrm{CO_3}^= = \mathrm{TIC}\alpha2$$

where

$$\alpha_0 = \left\{\frac{1 + K_1}{\mathrm{H}^+} + \frac{K_1 K_2}{[\mathrm{H}^+]^2}\right\}^{-1}$$

$$\alpha_1 = \left\{\frac{[\mathrm{H}^+]}{K_1 + 1 + K_2/[\mathrm{H}^+]}\right\}^{-1}$$

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doi:10.1016/j.chroma.2006.03.015

$$\alpha_2 = \left\{ \frac{[\mathrm{H}^+]^2}{K_1 K_2} + \frac{[\mathrm{H}^+]}{K_2 + 1} \right\}^{-1}$$

and K_1, K_2 are the dissociation constants of carbonic acid.

TAlk is defined as the sum of acid buffering components consumed during titration (e.g. bicarbonate, carbonate and organic acid anions) less the acidity already in solution. Assuming that the concentration of anions from organic acids is negligible TAlk is defined by the following equation:

$$\mathrm{TAlk} = 2\,[\mathrm{CO}_3^{2-}] + [\mathrm{HCO}_3^-] + [\mathrm{OH}^-] - [\mathrm{H}^+]$$

TAlk can be obtained by TIC and pH values, by substituting $\mathrm{CO_3}^{2-}$ and $\mathrm{HCO_3}^{-}$ in the alkalinity definition

$$\mathrm{TAlk} = \mathrm{TIC}\,[\alpha_1 + 2\alpha_2] + [\mathrm{OH}^-] - [\mathrm{H}^+]$$

This calculation needs the accurate knowledge of thermodynamic constants, the dependence on temperature and ionic strength of the equilibrium constants.

Alternatively the excess partial pressure of CO_2 ($E_p CO_2$) and TIC can be calculated from alkalinity and pH values. This procedure has been applied in studies on freshwater systems [5–7], but the calculation outputs have not been validated by direct measures of total inorganic carbon. In fact improving accuracy of carbon speciation in a water sample depends also on the availability of a reliable direct measure of total inorganic carbon.

In oceanographic campaigns, planned to evaluate the sinking capacity of oceans for CO_2, TIC was determined by automated methods based on sample acidification, CO_2 stripping followed by the measure of carbon dioxide by coulometric titration [8] or non dispersive-IR [9].

The use of chromatographic methods for carbonate determination has not been widely diffused. Since carbonate is the anion of a weak acid the chromatographic technique of choice was ion exclusion coupled with conductivity detection [10]. Carbonate was also determined in high purity water by IC after a preconcentration step [11], or by capillary electrophoresis [12], but few validation data have been reported.

A direct measurement of TIC is made possible by the introduction of electrolytic generated hydroxide eluent in ion chromatography which allows to detect a chromatographic peak for carbonate [13]. The advantage of this method is that all the inorganic forms of carbon are converted in carbonate in the basic eluent and can be detected as a single peak by conductivity detection. Because samples are filtered before injection, dissolved inorganic carbon is actually measured.

The aim of our work has been to test the feasibility of using ion chromatography as a reliable technique for the determination of TIC. Measurements carried out by IC on samples of Italian lakes and rivers are compared with TIC values calculated from alkalinity and pH values, taking into account temperature and ionic strength.

2. Experimental

2.1. Materials and chemicals

All solutions were prepared by dissolving salts of analytical grade in ultra pure (18 MΩ cm^{-1} quality) water produced by a Milli-Q system (Millipore, Bedford, MA, USA). Concentrated standard solutions were prepared from sodium hydrogen carbonate (Merck, Darmstadt, Germany) dried at 105 °C for 2 h and kept in a desiccator. Working standard solutions were daily prepared by dilution of these concentrated solutions with ultra pure water.

2.2. Ion chromatographic determination

Chromatographic analyses were performed on a DX-320 Ion Chromatograph (Dionex, Sunnyvale, CA, USA) equipped with AS50 Autosampler, GS50 Gradient Pump, LC25 column compartment and ED50 conductivity detector. Separations were carried out using a Dionex IonPac AS17 (250 mm × 4.0 mm) analytical column and an IonPac AG17 (50 mm × 4.0 mm) guard column.

Anions were detected using an electrochemically regenerated Atlas suppressor coupled to conductivity detection. Injection volume was 100 μl. Isocratic 12 mM KOH eluent was electrolytically generated at the flow rate of 1 ml min^{-1}using an EG40 Eluent Generator equipped with EluGen-OH cartridge and a continuously regenerated anion trap column.

All measurements were carried out at 35 °C and all samples were filtered through 0.45-μm filters. Dionex Chromeleon 6.40 chromatography software controlled data collection and the operation of all components in the system.

2.3. Total alkalinity determination

TAlk was determined by computer guided acidimetric titration using the Gran method [14] with Radiometer ABU91 and TIM900 automatic titrators. In the range 0–5 mequiv. l^{-1}, 30–50 ml of sample were titrated with 0.05N HCl [15].

2.3.1. Calculation of total inorganic carbon

TIC was calculated from TAlk, pH, ionic strength and temperature using the stoichiometric approach of inorganic carbon equilibrium [1].

$$\mathrm{TIC} = \frac{(\mathrm{TAlk} - K_\mathrm{w})/[\mathrm{H}^+] + [\mathrm{H}^+]}{a_1 + 2\alpha_2}$$

Because of the low TOC concentrations (all samples were below 5.0 mg C l^{-1} and 95% of the samples below 2.0 mg C l^{-1}), the influence of organic anions on alkalinity was considered negligible. The calculation took into account the dependence of the inorganic carbon (K_1, K_2) and water (K_w) equilibrium constants from temperature and ionic strength [1,5].