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A rapid method for determination of total dissolved inorganic carbon in seawater with high accuracy and precision

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Abstract

A rapid method for determination of total dissolved inorganic carbon (C_T) in seawater with high accuracy and precision has been developed. The method is based on continuous gas extraction of acidified seawater that is pumped through an extraction chamber at a constant flow rate. The purged carbon dioxide is determined with a NDIR gas analyser. A high accuracy was achieved by continually shifting between sample and a certified reference material in 2-min intervals. The method was compared with the current standard, the coulometric technique. Seawater samples having C_T-concentrations between 1950 and 2160 μmol kg^{-1} were analysed and the results for the two methods showed good correlation (linear regression equalled C_T^{coul}=1.0011*C_T^{NDIR}−4.28, R^2=0.99994). Precision was comparable, with the method presented having a standard deviation of 0.05% and the coulometric having 0.08%. However the proposed method is faster than the coulometric method having a rate of about 12 samples per hour using a sample volume of less than 50 ml. Furthermore the hazardous chemicals associated with the coulometric technique are not needed.

Keywords: Dissolved inorganic carbon; High-accuracy measurements; Seawater; Carbon dioxide; NDIR; Carbonate

1. Introduction

A potential climate change as a result of emission of anthropogenic carbon dioxide has received a lot of attention during the last decades (e.g. IPCC, 2001). About half of the carbon dioxide emitted from fossil fuel burning stays in the atmosphere, while the terrestrial biosphere and the oceans sequester the remaining part. One important aspect is the relative importance of these two pools as sinks for atmospheric carbon dioxide. In order to assess the concentration increase of total dissolved inorganic carbon (C_T) in the oceans, as a result of increased atmospheric carbon dioxide partial pressure (pCO$_2$), measurements of high accuracy and precision are needed. At present the annual atmospheric pCO$_2$ increase is in the order of 1.5 μatm, which correspond to an increase in C_T of about 1 μmol kg^{-1}, on a background of ~2000 μmol kg^{-1}, in a surface water of constant total

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alkalinity that is in equilibrium with the atmosphere. This increase is dependent on the temperature and the total alkalinity of the water, but the magnitude indicates the demand set on the analytical techniques if this signal is to be studied. Furthermore the effect of biological and physical processes on the C_T-concentration is generally small in relation to background concentrations.

High-accuracy measurements have been made possible by the technique where carbon dioxide is extracted from an acidified seawater sample of known volume and temperature followed by coulometric determination (Johnson et al., 1985, 1987). This technique was automated into a Single-Operator Multi-Metabolic Analyser (SOMMA) (Johnson et al., 1993) which since then has been the standard instrumentation for the determination of C_T. Even if this technique has good accuracy and precision in the lab as well as at sea, the time to analyse one sample is around 15 min. Together with a Certified Reference Material (CRM, supplied by A. Dickson, Scripps Institution of Oceanography USA) makes the throughput at ~3 samples per hour. Furthermore the coulometric detection requires a reagent based on a DMSO solution, making it less nice for the working environment.

Analytical techniques for the determination of C_T using non-dispersive infrared (NDIR) gas analyser detection have also been applied with different sample treatment. Examples are systems determining the CO_2 extracted out of acidified samples of known volume, similar to the SOMMA but with NDIR detection (e.g. Goyet and Snover, 1993; O'Sulivan and Millero, 1998), systems extracting CO_2 out of samples of small (0.1–0.6 ml) known volume that are acidified in flow mode followed by NDIR detection (Abdullah and Eek, 1995; Pérez-Ponce et al., 1998), and a fully automated, continuous flow-through analyser with NDIR detection (Kimoto et al., 2002). The first systems have similar precision and accuracy as the SOMMA, as well as time needed per determination. The determinations using smaller volumes have less precision and accuracy than the SOMMA, but are faster. The system described by Kimoto et al. (2002) is fast (down to one sample per minute) and precise, but the accuracy of their method is difficult to estimate.

In this contribution, we present a technique for determination of C_T in oceanic waters with a NDIR gas analyser at an accuracy and precision comparable to the SOMMA system, but at a rate of ~12 samples per hour using a sample volume of less than 50 ml. A significant difference compared to the SOMMA system is that this method does not require the use of hazardous chemicals.

2. Method

The presented method is based on continuous gas extraction of acidified seawater that is pumped through an extraction cell at a constant flow rate. The extracted carbon dioxide is determined by measuring its mole fraction in the gas with infrared detection (NDIR). The principle of this method is similar to Flow Injection Analyses, FIA (Ruzicka and Hansen, 1975), but continually compares the signal from a sample with the signal from a certified reference material (CRM). In practice this means that the CRM-signal constitutes the baseline signal. Given the small concentration range in samples makes it possible to keep the sample signal within a narrow range from this combined CRM/baseline signal. This in combination with the short time interval between the CRM measurements reduces the impact of potential errors due to variations in extraction efficiency and instrument imprecision. The critical aspects of this method are firstly to achieve a constant carrier gas and sample flow rate. Secondly sample flow rate out of the extraction cell must also be relatively constant. The design of the extraction cell is therefore essential. However, imprecision in the parameters above will be detected as a poor repeatability of the signal from the CRM making it easy to detect problems in the system.

A schematic diagram of the analytical system is shown in Fig. 1. Teflon, nylon and PVC tubing were used as carriers of the gas, water and acid. 1-µm PTFE filters (PALL, Gelman Laboratory, USA) were attached before the inlets to the NDIR detector to avoid aerosols entering the detector. The NDIR detector was "reset" before any sample was analysed by running the system in the analyzing mode, but without addition of the sample.