

Procedures for direct spectrophotometric determination of carbonate ion concentrations: Measurements in US Gulf of Mexico and East Coast waters



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ABSTRACT

Refined procedures were developed for directly determining carbonate ion concentrations in seawater through measurement of the ultraviolet absorbances of lead carbonate and chloride complexes after addition of divalent lead (Pb(II)) to a seawater sample. Our model algorithm is based on carbonate ion concentrations calculated from measurements of pH and dissolved inorganic carbon (DIC) obtained on a NOAA ocean acidification cruise (GOMECC-2, the second Gulf of Mexico and East Coast Carbon cruise). These calculated carbonate concentrations, in conjunction with Pb(II) absorbance measurements for the same seawater samples, were used to refine previous algorithms based on different chemical-measurement techniques and a limited range of carbonate concentrations. The precision of the spectrophotometric carbonate measurements is affected by the concentration of Pb(II) in the titrated seawater samples. Doubling the concentration of the titrant improved precision relative to previously published procedures but required formulation of a correction for changes in carbonate ion concentration caused by the titrant addition. Minor changes in the new algorithm for the spectrophotometric method produced carbonate ion values (at 25 °C) in excellent agreement with values calculated from paired pH and DIC observations over a carbonate concentration range of 73–258 $\mu\text{mol kg}^{-1}$. This new algorithm, tested on three subsequent research cruises in the Gulf of Mexico, showed a random scatter of residuals and an average offset between measured and calculated carbonate concentrations equal to $-0.92 \pm 5.33 \mu\text{mol kg}^{-1}$.

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1. Introduction

Documentation of the chemical changes accompanying ocean acidification is necessary for understanding the long-term changes in biogeochemical processes caused by anthropogenic influences on the global carbon cycle (Doney et al., 2009; Feely et al., 2012; Feely et al., 2004; Guinotte and Fabry, 2008; Kleypas and Yates, 2009; Millero, 2007). The most ecologically significant changes in seawater chemistry that accompany ocean acidification are the decreases in carbonate ion concentrations that have a major impact on calcifying organisms (Doney et al., 2009; Fine and Tchernov, 2007; Friedman et al., 2012; Guinotte and Fabry, 2008; Kleypas and Yates, 2009; McCulloch et al., 2012; Morse et al., 2007).

Rather than being directly measured, carbonate ion concentrations are generally calculated from any two of the four major CO₂ system parameters: pH, fugacity of CO₂ (*f*CO₂), dissolved inorganic carbon (DIC), and total alkalinity (TA) (Clayton et al., 1995). Byrne and Yao (2008) showed that total carbonate ion concentrations ($[\text{CO}_3^{2-}]_{\text{T}}$) can

be directly determined via spectrophotometric observations of lead carbonate complexation subsequent to direct addition of Pb(II) to seawater samples. Spectrophotometric carbonate ion determinations are analogous to pH measurements (Bellerby et al., 2002; Byrne and Breland, 1989; Clayton and Byrne, 1993; Tapp et al., 2000) and are equally rapid and robust. Spectrophotometric methods are advantageous due to the simplicity of the measurements and the comparatively low cost of the required instrumentation. Easley et al. (2013) demonstrated that minor changes to preexisting computational algorithms could result in improved agreement between spectrophotometrically measured $[\text{CO}_3^{2-}]_{\text{T}}$ and values of $[\text{CO}_3^{2-}]_{\text{T}}$ calculated from pH_T and DIC.

In this work we present procedures that improve upon the original spectrophotometric methods of Byrne and Yao (2008) and Easley et al. (2013). The original algorithm of Byrne and Yao (2008) was improved by using field data obtained with state-of-the-art measurement methods in the Gulf of Mexico and Atlantic Ocean coastal waters of the United States. Easley et al. (2013) provide $[\text{CO}_3^{2-}]_{\text{T}}$ measurements that are in excellent agreement with $[\text{CO}_3^{2-}]_{\text{T}}$ values calculated from measurements of pH and DIC for carbonate concentrations between 38 and $\sim 180 \mu\text{mol kg}^{-1}$. The procedures used in this work were aimed at extending direct spectrophotometric measurements of $[\text{CO}_3^{2-}]_{\text{T}}$ to concentrations well above $180 \mu\text{mol kg}^{-1}$. A more concentrated titrant was used to provide higher

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lead concentrations and improve signal-to-noise ratios. An accompanying correction procedure was also developed to account for the CO₂ system perturbations created by adding the Pb(II) titrant to the seawater. The accuracy of the updated algorithm was evaluated using data obtained on three subsequent cruises in the Gulf of Mexico.

1.1. Analytical background

Direct measurements of [CO₃²⁻]_T in seawater can be obtained via observations of lead carbonate complexation spectra in the ultraviolet. Ratios (*R*) of absorbances (*A*) measured at two wavelengths (234 and 250 nm) are used to calculate [CO₃²⁻]_T:

$$R = \frac{250A}{234A} = \frac{250\epsilon_{\text{Pb}} + 250\epsilon_{\text{PbCO}_3} \text{CO}_3\beta_1 [\text{CO}_3^{2-}]_T}{234\epsilon_{\text{Pb}} + 234\epsilon_{\text{PbCO}_3} \text{CO}_3\beta_1 [\text{CO}_3^{2-}]_T} \quad (1)$$

where ϵ_{xy} is the molar absorptivity for species *y* at wavelength *x*. The formation constant of lead carbonate is given as $\text{CO}_3\beta_1$, and [CO₃²⁻]_T is the total concentration of carbonate ion.

Eq. (1) can be rearranged as:

$$-\log [\text{CO}_3^{2-}]_T = \log \left(\frac{\text{CO}_3\beta_1}{e_2} \right) + \log \left(\frac{R - e_1}{1 - R \frac{e_3}{e_2}} \right) \quad (2)$$

The parameters *e*₁, *e*₂, and *e*₃/*e*₂ are dependent on salinity and are expressed as follows:

$$e_1 = \frac{250\epsilon_{\text{PbCO}_3}}{234\epsilon_{\text{PbCO}_3}}, \quad e_2 = \frac{250\epsilon_{\text{Pb}}}{234\epsilon_{\text{PbCO}_3}}, \quad e_3 = \frac{234\epsilon_{\text{Pb}}}{250\epsilon_{\text{Pb}}} \quad (3)$$

The salinity-dependent stability constant for formation of the lead carbonate complex, PbCO₃⁰, is given as:

$$\text{CO}_3\beta_1 = \frac{[\text{PbCO}_3^0]}{[\text{Pb}^{2+}]_T [\text{CO}_3^{2-}]_T} \quad (4)$$

where [Pb²⁺]_T represents the total concentration of all non-carbonate lead species (i.e., Pb²⁺, PbCl_n).

The *e*₃/*e*₂ ratio is obtained in solutions with low pH where no influence from CO₃²⁻ complexation is observed (Byrne and Yao, 2008) and is directly measured as a quotient of Pb(II) absorbances (*e*₃/*e*₂ = 234*A*/250*A*). The salinity-dependent *e*₁ and $\text{CO}_3\beta_1/e_2$ parameters are determined through iterative analyses of Pb(II) spectra over a range of calculated carbonate ion concentrations.

2. Methods

2.1. GOMECC-2 cruise measurements

The 2012 Gulf of Mexico East Coast Carbon (GOMECC-2) study was performed over a period of 23 days onboard the NOAA Ship *Ronald H. Brown* in the Gulf of Mexico and along the East Coast of the United States (Fig. 1). During this research cruise, [CO₃²⁻]_T, pH_T, DIC, TA, *f*CO₂, nutrients, salinity, temperature, and depth of sample collection were measured (Wanninkhof et al., 2014). Measurement procedures and thermodynamic relationships for these parameters (excluding spectrophotometric [CO₃²⁻]_T) are given in Dickson (2007). The pH indicator used on GOMECC-2 was purified meta-cresol purple (*mCP*) (Liu et al., 2011; Patsavas et al., 2013; Yao et al., 2007). GOMECC-2 sample characterizations that did not contain the full suite of CO₂ system parameters (pH, DIC, TA, *f*CO₂) were not used in this work. The resulting data set contained 885 observations of pH_T, DIC, TA, and *f*CO₂. Using the paired pH_T and DIC measurements to calculate [CO₃²⁻]_T for each sample yielded

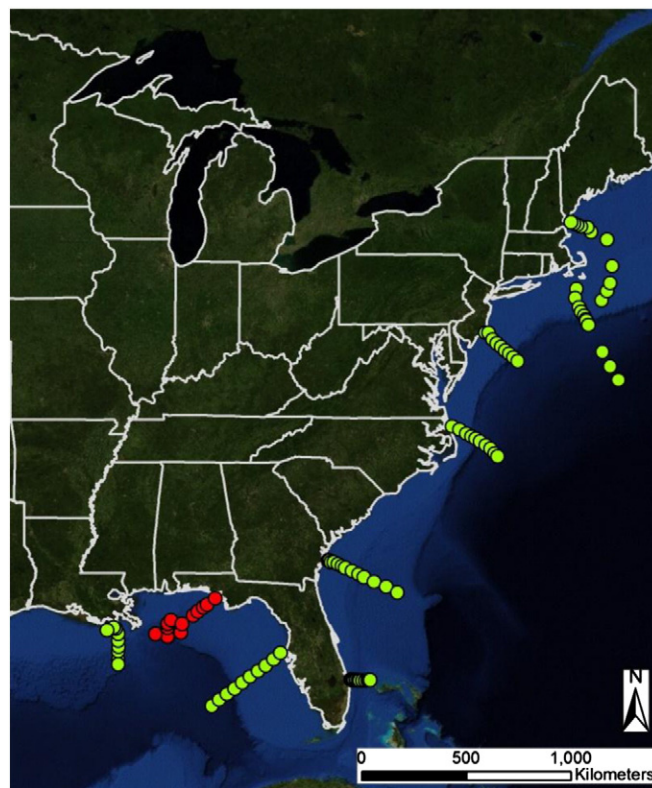


Fig. 1. Sample locations. The 2012 GOMECC-2 stations are shown in green. The 2013 Gulf of Mexico cruise stations are shown in red.

a [CO₃²⁻]_T data set (*N* = 885) with an uncertainty on the order of 2 μmol kg⁻¹.

2.2. Spectrophotometric [CO₃²⁻]_T field measurements

Direct spectrophotometric measurements of [CO₃²⁻]_T were performed using procedures similar to those outlined in Byrne and Yao (2008) and Easley et al. (2013). Sample seawater was collected in 10 cm pathlength quartz optical cells without contact with the atmosphere. The cells were capped with Teflon stoppers to prevent air exchange. The cells were warmed in a custom aluminum heat-exchanger attached to a recirculating water bath maintained at 25 ± 0.01 °C. After the samples were equilibrated to 25 °C, each cell was transferred to a custom water-jacketed cell holder in an Agilent 8453 UV–Vis spectrophotometer. A reference spectrum was recorded, and after 20 μL of 0.022 M lead perchlorate (Pb(ClO₄)₂) was added to the sample cell (final concentration: 1.52 × 10⁻⁵ mol kg⁻¹), absorbances at 234 and 250 nm were recorded six times and averaged. It should be noted that both Byrne and Yao (2008) and Easley et al. (2013) used lead chloride as the titrant. In this study lead perchlorate, which is more soluble than lead chloride, was used (Fisher Scientific, 99.99% purity). As a result, the lead concentrations of the analyzed seawater samples were approximately twice that of the previous methods.

2.3. Parameterization procedure

CO₂ system calculations were made using CO2SYS version 2.1 (Pierrot and Wallace, 2006). Because spectrophotometric pH_T is determined on the total hydrogen ion scale (Liu et al., 2011), the dissociation constants of Lueker et al. (2000) were used. Other parameters and relationships selected for the CO2SYS runs included *K*_{H2SO4} from Dickson et al. (1990) and the total-boron-to-salinity ratio from Lee et al. (2010). After obtaining [CO₃²⁻]_T values calculated at 25 °C from

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