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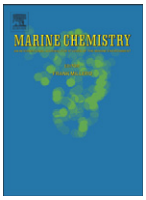

Modifications of the curcumin method enabling precise and accurate measurement of seawater boron concentration

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ABSTRACT

To achieve greater precision and accuracy in the measurement of seawater boron concentrations, we propose a series of modifications to an established (curcumin) method based on the reaction of boric acid with curcumin. The modifications were derived from a series of experiments evaluating the stability of the curcumin–acetic acid reagent, the dependence of the reaction on temperature and duration, the effect of evaporation during the dehydration process, the interference of water, and the effect of sea salts. Application of the modified method to analysis of seawater samples collected from the Pacific Ocean indicated that it yielded considerably better precision and accuracy for boron concentration measurements than both the conventional curcumin method and other analytical techniques.

1. Introduction

Measurement of aqueous boron (B) at levels of parts per million is of great interest to water research scientists. For example, a lifetime human health advisory level of 0.6 mg B L^{-1} for drinking water was considered appropriate in the past, but B in drinking water has recently come to the attention of the U.S. Environmental Protection Agency as a contaminant potentially needing regulation (Parks and Edwards, 2005). For irrigation water, as little as 0.5 mg B L^{-1} may be harmful to certain crops (Goulden and Kakar, 1976).

The concentration of B in seawater varies with chlorinity (Cl, ‰) in a conservative manner, and no chemical or biological processes affecting the B/Cl ratio in ocean waters have yet been identified (Park and Schlesinger, 2002). Relative to the global overturning circulation time scale (~1000 years), the considerably longer residence time of B (10–20 million years) also points to its conservative nature in seawater (Lemarchand et al., 2000). Boron is one of the major dissolved components in seawater, with concentrations of 4–5 mg L^{-1} in open ocean waters, where it occurs as boric acid, $B(OH)_3$ and borate, $B(OH)_4^-$. The equilibrium reaction between these two B species contributes to pH buffering in seawater, and borate is the third largest contributor to total alkalinity $(=[HCO_3^-]+2[CO_3^{2-}]+[B(OH)_4^-]+$ minor components $-[H^+])$ after bicarbonate and carbonate. Therefore, accurate estimation of the borate contribution to total alkalinity is critical in converting total alkalinity to carbonate alkalinity $(=[HCO_3^-]+2[CO_3^{2-}])$, and vice versa (Lee et al., 1997). To estimate borate alkalinity in seawater, both accurate dissociation constants for boric acid in seawater and accurate seawater B concentration data are needed (Dickson, 1990; Roy et al., 1993). In these calculations, the uncertainty (±0.005) associated with the mean B (mg kg^{-1}) to Cl (‰) ratio of 0.232 (Uppström, 1974) results in concentration errors of several µM in predictions of borate alkalinity using chlorinity data. This B/Cl ratio was derived from only 20 measurements made on tropical Pacific Ocean samples, but nonetheless has been widely used for estimating seawater B concentrations in conjunction with chlorinity data (e.g., Lee et al., 1997; Jimin et al., 2007). Recently, the importance of measurement of seawater B concentrations has been recognized, as the B isotope composition of marine carbonates is used to reconstruct past variations in ocean chemistry and atmospheric CO_2 (Lemarchand et al., 2000; Zeebe and Wolf-Gladrow, 2001; Jimin et al., 2007). The interpretation and applications of marine carbonate and B chemistry are dependent on reliable data on seawater B concentrations.

Over recent decades there have been significant advances in B analysis techniques (Sah and Brown, 1997), but more precise and accurate methods for seawater B analysis are needed to ensure long-term measurement reproducibility, since existing methods involve substantial uncertainty (Table 1). Some novel and sensitive approaches employ either inductively-coupled plasma optical emission (ICP-OES) or mass (ICP-MS) spectrometry, both of which are difficult and expensive to use. Furthermore, these methods are subject to matrix effects due to

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Table 1
Partial list of published seawater B concentration analysis methods.

Year	Authors	Methods	Precision (%)	Accuracy (%)
1958	Gast and Thompson	Mannitol titration[a]	More than ±4[b]	Not given
1960	Parker and Barnes	Fluorimetry	±2	Not given
1962	Greenhalgh and Riley	Curcumin	±0.45	Not given
1971	Nicholson	Nile blue A	±3.5	Not given
1974	Uppström	Curcumin	±0.9 to ±1.6	0.2 to 2.6
1978	Kuwada et al.	DNNDO	Not given	0.6 to 1.2
1984	Oshima et al.	DBC	±0.67	0.9 to 3.8
1993	Lopez et al.	Azomethine-H Curcumin Carmine	±0.96 (azomethine-H) ±1.96 (curcumin) ±6.8 (carmine)	3 to 7 (azomethine-H)
1997	Susanne	NTIMS, ICP-OES	±2 (NTIMS) ±5 (ICP-OES)[c]	Not given
2003	Youssef	Curcumin	±2.2	Not given
2006	Şahin and Nakiboğlu	Voltammetry	±5.1	4 to 8
2007	Ramanjaneyulu et al.	Chemical PGNAA	±5	5

[a] Yielded the poor accuracy and precision and was widely used by scientists prior to 1960s (Greenhalgh and Riley, 1962).
[b] Provided by Greenhalgh and Riley (1962).
[c] Matrix effects could result in errors in the order of 10 to 20% (Susanne, 1997).

the presence of salts, or memory effects from the spray chamber and the cones (Sah and Brown, 1997; Susanne, 1997). To minimize such adverse effects, these methods require additional analytical procedures including sample extraction, purification and dilution, all of which increase analysis time and difficulty, and may introduce errors. Because of these shortcomings, they are not suitable for routine B analysis. Reliable protocols for seawater B concentration measurement using ICP-OES or ICP-MS are not yet fully developed, and in the few attempts made to date, large uncertainties have been identified (Susanne, 1997).

Most commonly documented methods for seawater B analysis are based on spectrophotometry, because it is simple and cost effective. Among these are the curcumin (Greenhalgh and Riley, 1962; Uppström, 1968; Dyrssen et al., 1972; Youssef, 2003), carmine (Grasshoff et al., 1983; Lopez et al., 1993; Eaton et al., 1995) and azomethine-H methods (Lopez et al., 1993; Harp, 1997) (see Table 1). The major difficulties associated with the application of these methods to natural water samples are interference of some dissolved species, and low sensitivity and precision (Sah and Brown, 1997). The curcumin method is more sensitive and reliable than the other spectrophotometric methods (Dyrssen et al., 1972), and is a widely accepted procedure for measuring B concentrations in seawater (Grasshoff et al., 1983) and other natural waters (Eaton et al., 1995). It is also widely used in the fields of food science, nuclear energy, pharmacy, metallurgy, agriculture, and tissue biology.

A spectrophotometric curcumin method applicable to seawater B analysis was first developed by Greenhalgh and Riley in 1962, and a series of modifications were subsequently proposed (e.g., Hayes and Metcalfe, 1962). Following thorough evaluation of those modifications, Uppström proposed a simple protocol for determination of B in seawater (Uppström, 1968). The protocol has several key advantages over the other methods, including that it minimizes the interference of water in the reaction between boric acid and curcumin by removal of water from seawater samples by reaction with propionic anhydride, catalyzed by oxalyl chloride in such a way as to avoid distillation and evaporation processes. Water removal allows the reaction between B and curcumin to take place in a homogeneous liquid medium. The Uppström protocol is less time consuming, simpler and more accurate than other methods. However, this protocol has yet to be fully evaluated over a wide range of experimental conditions.

In the present study we assessed the Uppström protocol in terms of several key factors (the stability of curcumin–acetic acid reagent, reaction temperature and duration, evaporation during the dehydration process, the water interference and the interference of sea salts), all of which are critical in forming the boron–curcumin complex. We consequently present a set of modifications that yield more accurate and precise measurements of seawater B concentrations.

2. Experimental

2.1. Apparatus

An Agilent 8453 UV–visible spectrophotometer (1 cm optical cell) was used to measure the absorbance at 543 nm. Adjustable micropipettes (Eppendorf) delivering volumes of 100 μL, 500 μL, 1000 μL and 5000 μL, were used to add samples and reagents to 50 mL screw cap polyethylene reaction bottles. The samples and reagents were delivered to an accuracy of ±0.2% using the micropipettes. One liter polyethylene volumetric flasks (Nalgene) were used in the preparation of dilutions. To avoid possible B contamination, borosilicate glassware was not used in any analytical step (Grasshoff et al., 1983). A recirculating water bath (Jeio Tech.) was used to keep samples to a constant temperature during reactions. The salinity of seawater samples was determined using a salinometer (Model 8410A, Portasal) with an analytical accuracy of ±0.003 and precision of ±0.0003. The corresponding chlorinity values were calculated using the salinity to chlorinity ratio of 1.80655 (Cox et al., 1967).

2.2. Reagents

All reagents (Sigma-Aldrich) were of analytical grade unless stated otherwise. Milli-Q water used in preparing solutions was obtained from an AW-1001UP automatic pure water distillation apparatus and ultra pure water system (Top Trading Corp., Korea). Curcumin–acetic acid reagent was prepared by dissolving 0.125 g of curcumin in 100 mL of glacial acetic acid. Sulfuric–acetic acid reagent was prepared by mixing equal volumes of concentrated sulfuric acid and glacial acetic acid. Propionic anhydride (99%) and oxalyl chloride (98%) were used for dehydration. One liter of buffer solution was prepared in a 1 L flask by mixing 135 mL of glacial acetic acid with 90 mL of ethanol (99.9%, J.T. Baker) and 180 g of ammonium acetate (Merck), and diluting to 1 L with Milli-Q water. A standard stock solution of boric acid (100 mg L^{-1}) was made by dissolving 0.5717 g of boric acid (99.999%) in Milli-Q water (final volume 1 L). The bottle was kept sealed to prevent absorption of atmospheric moisture, and the solution was discarded 2 months after preparation. Daily B measurements involved five working standard solutions of known B concentration (1–5 mg B L^{-1}), prepared by appropriate dilution of the standard stock solution, and a blank solution without B.

Most reagents were weighed to an accuracy of ±0.0001 g. The boric acid salt for preparation of the standard stock solution was weighed to an accuracy of ±0.00001 g. Correction for air buoyancy was applied to all weight measurements.