



Spectrophotometric Determination of Boron in Saltwater Using Azomethine H and Ferroin Reagents

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ABSTRACT

Analysis of boron concentration is increasing gaining interest owing to the importance of boron in plants and animals nutrition. Boron is a micronutrient in plant nutrition with role in strengthen of cell wall. Studies have also suggested that boron reduces risk of diabetes in human. However, boron toxicity has also been established in both plants and animals. This has necessitated legislation of permissible level of boron. A number of methods have been employed in the analysis of boron in different samples. Spectrophotometric methods have been widely used for routine boron analysis. The effectiveness of two extraction reagents for boron analysis were compared. Extraction of boron as boric acid was carried out using ferroin and azomethine H reagents. Samples were collected from saltwater sources. The ferroin borodisalicylate complex and 1, 3 bischelate boron complexes were measured at fixed wavelengths of 410 and 516 nm respectively. The result obtained for boron concentration range from 3.69 ± 0.04 to 4.98 ± 0.09 ppm with ferroin method while 2.80 ± 0.10 to 4.87 ± 0.08 ppm with azomethine H method. A p-value of 0.792 was obtained when t-test was conducted. Result of statistical analysis showed that boron concentrations of the methods used were not significantly different. The result of this research shows that boron concentration in salt and freshwater using extraction reagent. It shows that boron levels in the natural water is within the permissible level.

Keywords: boron, ferroin borodisalicylate, azomethine H, bischelate

INTRODUCTION

Boron is an element that is found abundant in nature in combined forms as in the environment as borates, borosilicates and boric acid (Bryjak, Wolska, & Kabay, 2008). Factors such as soil geochemistry, water sources, rocks and local anthropogenic activities causes variation in boron concentration. The concentration range of 0.0001 to 10 ppm has been reported for environmental boron (Victor *et al.*, 2015). In water, boron exists in two forms, as boric acid or tetrahydroxyborate (1-) ion. It is reported the global range of boron in seawater is from 0.5 to 9.6 ppm with an average of 4.5 ppm (Schubert, 2003). It was reported that boron concentration in seawater varies with total salinity and chlorinity (Lee *et al.*, 2010). The range of boron concentration in freshwater boron is from lower than 0.01 to 1.5 ppm (WHO, 1998). This variation is caused by factors such as proximity of coastal region, presence of boron rich deposits, drainage geochemistry and local anthropogenic activities. Boron concentration of about 360 ppm has been reported in Turkish area

of high boron reserve (William, 1994).. Precipitation and soil and underground water drainage are the main boron inputs into freshwater (Kabay *et al.*, 2015)

Methods used for boron analysis

Over the years, several analytical methods have been employed in the analysis of boron and these include colorimetric methods, atomic absorption spectroscopy, potentiometric methods, and neutron sources (Sah and Brown, 1997). Plasma and chromatographic technique such as high-performance liquid chromatography and ion chromatography have also been reported. Colorimetric methods employed for the determination of boron in water are based on the colorimetric reaction of the oxy-boron complex with different reagents such as ferroin, carmic acid, curcumin and azomethine-H (Kabay *et al.*, 2015). The optical density of the solution is measured at a particular wavelength and this is

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usually a function of the boron in solution. In this work, boron concentration was determined with ferroin and azomethine-H methods. However, other spectrophotometric methods will be briefly discussed.

The carmine method

Victor *et al.*, (2015), in their review of the chemistry of boron in water, reported that the carmine method is usually employed for boron analysis of a concentration range of 1 to 10 ppm. The method is based on the formation of a blue coloured boron complex with a carmine indicator in the presence of concentrated sulphuric acid. The optical density is measured at a wavelength of 605 nm. However, this method is not suitable for routine analysis because it requires the use of concentrated sulphuric acid (Potter and Lovelance, 1984).

The curcumin method

The curcumin method is usually employed for the analysis of food and water materials with a boron concentration of 0.1 to 1.0 ppm. This method is based on the reaction of curcumin (diferuloylmethane [C₂₁H₂₀O₆]) with boric acid to form red coloured complexes (Kabay *et al.*, 2015). These complexes are rosocyanin and rubrocurcumin (Spicer and Strickland 1939). The rosocyanin complex is formed from the reaction of boric acid and curcumin in the presence of sulphuric acid. The complex is usually a red coloured complex formed in a 1:2 reaction of boric acid and diferuloylmethane. The absorbance of the complex is measured at a wavelength of 545 nm. On the other hand rubrocurcumin is formed by the reaction of boric acid, curcumin and oxalic acid in a 1: 1: 1 stoichiometry. The rosocyanin is usually the more preferred complex for the determination of boron because it is more stable to hydrolysis and



Scheme 1: Formation of ferroin borodisalicylate complex. (Mathews, 1974)

The azomethine-H method

Capelle in 1961 suggested azomethine-H as a reagent for the analysis of boron. This reagent can be directly applied in an aqueous acidic medium and has been widely used for the spectrophotometric determination of boron in different matrix such as plants, siliceous material and water (Lopez *et al.*, 1992; Sah and Brown, 1997; Zajun *et al.*, 1999). Lopez *et al.* (1992) reported their work on the comparison of azomethine-H with carmine and curcumin

it has molar absorptivity that is twice that for rubrocurcumin (Spicer and Strickland, 1939; Victor *et al.*, 2015). Anions such as fluoride, nitrite and nitrate interfere with boron analysis with curcumin method (Matsuo *et al.*, 2004).

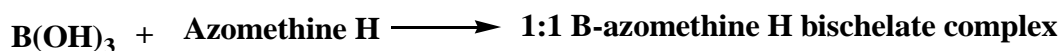
The ferroin method

The ferroin method is a solvent extractive method used for the spectrophotometric determination of boron in water as boric acid. This method was developed on the assumption that boron is generally present in low concentration in water sources and sewage. Basset and Matthews (1974) developed the ferroin method for boron analysis of the concentration range of 0.01 to 2.70 ppm and reported a detection limit of 0.027 ppm. However, they failed to suggest a limit of quantification for the ferroin method. The ferroin method is less sensitive and less selective and not suitable for analysis of samples of particularly low concentration of boron such as freshwaters that usually contain low concentrations of boron, when compared to the azomethine-H method. The method is based on the extraction of boron as ferroin borodisalicylate salt, an orange coloured complex which is usually insoluble in water but soluble in organic solvents. However, the salts can be extracted into chloroform and washed with water to remove ferroin salicylate and the absorbance of ferroin borodisalicylate solution is then measured at 516 nm using a UV/Vis spectrophotometer (Harp, 1997). This method suffers from interference from chloride ions above 1000 ppm and phenol of 10 ppm which are usually present in natural water. Scheme 1 shows the formation of ferroin borodisalicylate from boric acid and salicylate through borodisalicylate ion and ferroin ion.

methods for the analysis of boron in water and found the azomethine-H method to be the most sensitive, with a detection limit of 0.02 ppm and also the most selective (*i.e.* no interference was observed for the commonly occurring ions in water). The method gave 99 to 107 % recovery when the standard addition was carried out. The azomethine-H method is very suitable for routine boron analysis because it can be applied in a dilute acidic solution which is unlike most reagents usually employed for boron analysis,

which involves hazardous experimentation due to the use of concentrated acids, and it is also less time consuming (Oxspring *et al.* 1995; Sah and Brown, 1997; Zaijun *et al.*, 1999; Mohammed *et al.*, 2014). Studies have been conducted to determine the optimal conditions for quantifying boron using azomethine-H as a colouring agent, and also to understand the mechanism of interaction of azomethine-H and

boric acid. The observations from these studies proved that boric acid and azomethine-H interacts to form a coloured complex in solution which absorbs at 410 nm at pH of about 5.1 (Lopez *et al.* 1997; Matsuo *et al.* 2004) Evidence from NMR studies suggests that the complex formed is a 1:1 bischelate complex with tetrahedral boron, through the full processes illustrated in Scheme 2 (Matsuo *et al.*, 2004).



Scheme 2: Interaction of boric acid with azomethine-H to form a coloured compound (Matsuo *et al.*, 2004).

METHODOLOGY

Sampling

Water samples were collected from ten (10) locations of natural seawater sources of north Wales. The sample locations include Rhos on Sea, Llandudno, Penmaemwr, Menai Bridge, Llanfairpwll PG, The Swellies, Bangor Pier, Conway, Holyhead and Llanfairfechan. Samples were collected in 500 ml plastic bottles.

Azomethine-H method

A 5 mL water sample was measured into a 15 mL polypropylene centrifuge tube and 4 mL buffer masking solution and 2 mL of the azomethine-H solution were then added. The tube was placed on vortex mixer SAB (BioCote) for about 10 seconds at 1800 rpm for the solution to mix thoroughly. The solution was allowed to stand for about 60 to 120 minutes in fume cupboard before analysis.

UV Analysis

The absorbances of 1:1 bischelate azomethine boron complex was measured against water as reference at a fixed wavelength of 410 nm while ferroin borodisalicylate complex was measured against chloroform at a wavelength of 510 nm using a Perkin Elmer UV/Vis Lambda 35 spectrophotometer.

Standard Solution

Boron concentrations 0.27, 0.68, 0.95, 1.35, 2.03 and 2.70 ppm were used for plotting calibration

curve for the ferroin method. For the azomethine H methods 1, 2, 3, 4 and 5 ppm, were used. In both cases, deionised water was used as sample blank.

RESULTS AND DISCUSSIONS

Calibration plot for boron concentration in water

The calibration plots obtained by plotting absorbance and intensities of standard boric acid solution of known concentrations of boron are shown in Figures 1 (the ferroin method) and 2 (the azomethine-H method).

The limits of detection of boron found were 0.09 and 0.04 ppm for the ferroin and the azomethine-H methods while 0.10 and 0.08 ppm were obtained as limits of quantification for the ferroin and azomethine-H respectively as presented in Table 1. It also shows that the correlation of coefficient (R^2) of the azomethine H method (0.9997) is greater than that ferroin method (0.9961). Dynamic range found for ferroin method was between 1.00 to 2.00 ppm as large deviation was observed for boron concentration lower than 1 ppm and also for values greater than 2.0 ppm. With the azomethine H method 0.08 to 3.00 ppm was found as range for which minimal deviation was observed for boron concentration.

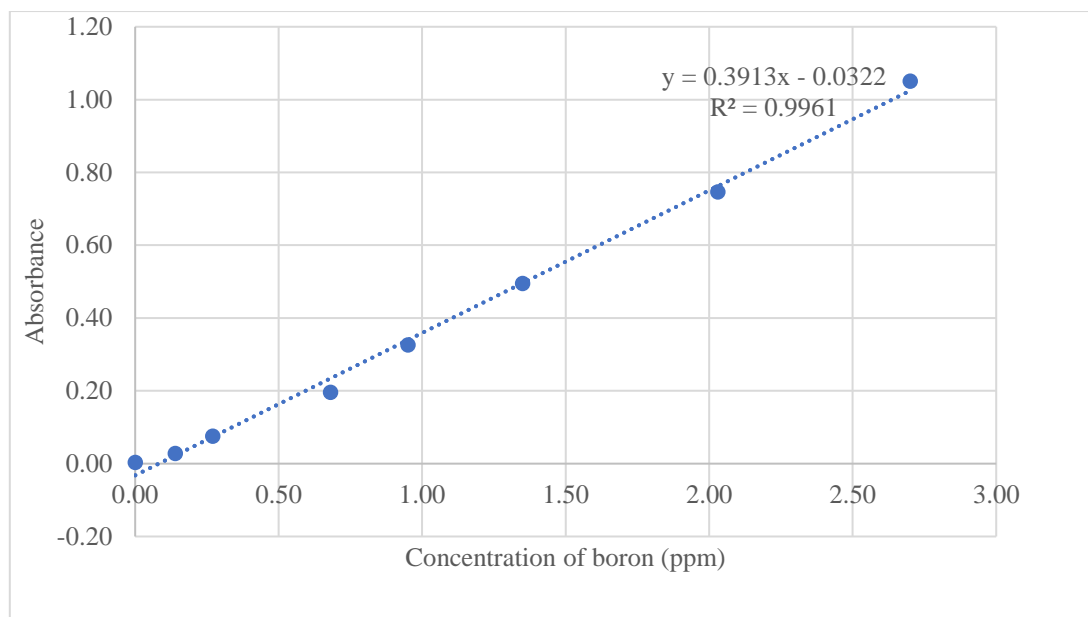


Figure 1: Linear plot of absorbance against concentration of boron (ppm) of the ferroin method.

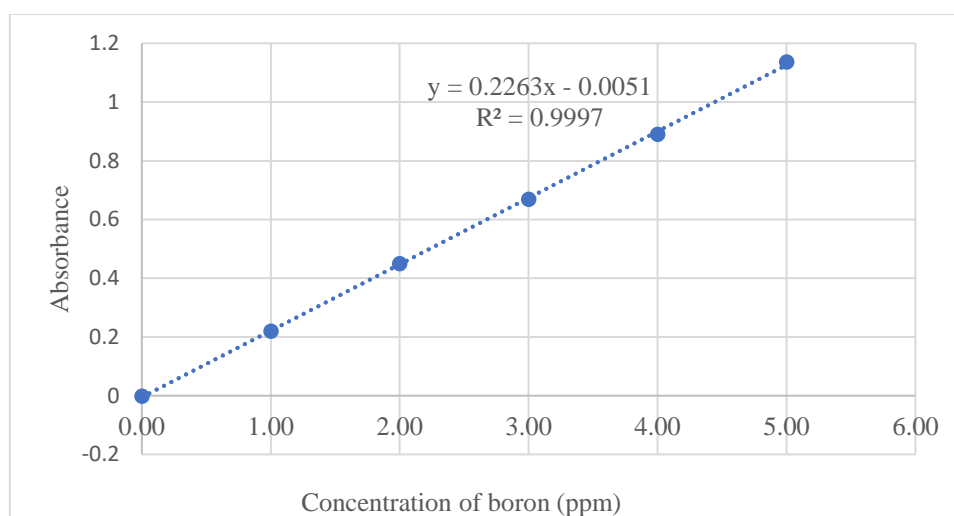


Figure 2: Linear plot of absorbance against concentration of boron (ppm) of the azomethine-H method.

Table 1: Comparison of parameters obtained from calibration plot

Parameter	Ferroin	Azomethine H
LOD (ppm)	0.09	0.04
LOQ (ppm)	0.1	0.08
R ²	0.9961	0.9997
Dynamic Range (ppm)	1.00 - 2.00	0.08 - 3.00

Error analysis was carried out to estimate the magnitude of errors in the measured values as a result of the number of steps associated with the experimental processes of the analytical methods used. The results were presented as mean concentration of replicate measurements with the standard error of the mean.

The concentrations of boron determined from samples collected at coastal sites range from 3.69 ± 0.04 ppm (Conwy) to 4.98 ± 0.09 ppm (Rhos on Sea) as illustrated in Table 3.2 were obtained for the ferroin method. With the azomethine-H method concentrations obtained range from 2.80 ± 0.10 ppm (Conwy) to 4.87 ± 0.08 ppm (Rhos on Sea) as given in Table 3.2. The values obtained agreed with literature data for global boron concentrations in seawater of 0.5 to 9.5 ppm and are similar to those found in seawater around Britain and Spain (4 to 5 ppm) reported by Mathews (1974) and Lopez (1992) using similar methods. The results agree the findings of Krishnan *et al.* (2013) using inductively coupled plasma-quadrupole mass spectrometry.

Table 2: The result of boron concentrations in seawater samples

Sample	B concentration (ppm)	
	Ferroin method	Azomethine H
Rhos on Sea	4.98 ± 0.09	4.87 ± 0.08
Llandudno	4.96 ± 0.14	4.20 ± 0.13
Penmaemwr	4.86 ± 0.03	3.95 ± 0.04
Menai Bridge	4.98 ± 0.08	3.71 ± 0.03
Llanfairpwll PG	4.69 ± 0.08	4.02 ± 0.14
The Swellies	4.80 ± 0.01	3.68 ± 0.05
Bangor Pier	4.54 ± 0.03	3.87 ± 0.02
Conway	3.69 ± 0.04	2.80 ± 0.10
Holyhead	4.49 ± 0.04	4.65 ± 0.06
Llanfairfechan	4.74 ± 0.11	3.64 ± 0.05

A t-test was conducted on the results from the azomethine-H and ferroin methods to test if there is a significant difference at 5 % level (*i. e.* $p = 0.05$). The probability value ($p = 0.792$) obtained was greater than 0.05. This implies that the results of the two methods were not statistically significantly different and the observed differences are attributed only to random error. The variation of boron concentration found for the samples with the colorimetric methods (Table 2) is possibly due

to matrix interference. The ferroin method suffers from interference such as phenol, chloride among other ions which are usually present in natural water in high concentrations. Excess ferroin and ferric salicylate which remain after back washing and filtration are other species that may possibly interfere when using this method. In addition, sensitivity of the ferroin method is reduced due to the multiple number of steps involved in this procedure.

Variation of boron concentration in the sampled areas is due to factors such as interaction between sea-fresh water interactions. Areas where these interactions occur causes an abnormality in the expected boron concentrations. For example, the concentration of boron at Conway is lower than expected because of influence of Gyffin river. While concentration at Llanfairfechan sea is low due to interaction of River Llanfairfechan.

Another factor that causes variation in boron concentration is the presence of natural absorbent materials such as mineral and plant materials that originates from decaying dead plants and weathering of rocks. Examples of such minerals that absorb boron include red mud, sepiolite, alunite and calcite. While residues from seed, wheat, rice and walnut are plant materials that adsorb boron. Calcium alginate and chitosan are biopolymers that remove boron from aqueous phase. It is reported that boron interacts chemically with these materials (Nasef *et al.*, 2014).

Conclusion

Boron is found as boric acid or tetrahydroxyborate(1-) ion in seawater. The concentration can be carried out using, a number of methods have been used for routine analysis. Colorimetric reagents ferroin and azomethine H have been used for extraction of boron complexes prior UV/ Vis analysis. The result of this work shows that azomethine method was more sensitive, cheap and convenient for routine boron analysis. However, results of statistical analysis showed that the of boron concentrations of the two methods were not significantly different at 95 % confidence interval.

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