Analytical Determination of Boron in Irrigation Water Using Azomethine-H: Spectrophotometry

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Abstract: *Boron level in irrigation water is an important factor for high yield and quality agricultural production. Concentration below 1ppm provides plants with proper development and higher concentration poses toxicity problem. This necessitates for the use of accurate technique for assessment of boron in the irrigation water. Several analytical methods have been used for determination of boron in water and waste water systems but optimization of measurement condition has not been fully carried out. Analytical method was developed using azomethine-H. Effect of ascorbic acid and pH were investigated. From the result obtained, it was found that ascorbic acid in the reagent serves as antioxidant and optimum pH for measurement was found to be 5.24 ± 0.02 at room temperature and wavelength of 415nm. This method showed wide linearity of up to 3ppm boron, good sensitivity and accuracy with limit of detection of 0.0514ppm within 95% confidence level. It can be concluded that this technique is better effective than the existing methods for boron determination in aqueous solution.*

Keywords*: Boron, Spectrophotometry, Azomethine-H, Irrigation-water, Absorbance*

I. Introduction

Boron is an essential element for plant growth at low concentration. Its functions include cell wall growth and improvement, cell division, fruit and seed development, sugar transportation and hormone development. Required concentration of boron in water represents an important factor for high yield and quality agricultural production [1].Boron concentration below 1ppm provides plants with proper development and higher concentration poses toxicity problem [2]. This therefore requires accurate technique for determination of boron level in water for agricultural production.

Analytical procedure provides means of assessing and monitoring of substance or substances in environment, water, soil and biological materials in both qualitative and quantitative terms. The qualitative findings establish the presence of a particular analyte in a sample while the quantitative is concern with amount of analyte in the specimen. Several methods are available for detecting boron in aqueous environments which can be classified as plasma based technique, mass spectrometry technique, ionometric approach and spectrophotometry method [3]. Each of these methods has advantages, disadvantages and limits of detection. Therefore, prior knowledge of concentration range of analyte in the sample to be investigated is needed in order to select appropriate analytic method.

Plasma based method also known as inductively coupled plasma (ICP) converts the boron species in the sample to elemental boron, further ionizes it to B^+ and then examined through detectors such as optical emission spectroscopy (OES), mass spectroscopy (MS). In the ICP-OES, wavelength of radiation released from the energized particles represents the properties of the element [4]. The ICP-MS determines boron by measuring the mass to charge ratio of the ion which gives both concentration and the stable isotope [3]. In general, this method has been utilized for samples from seawater, fresh water [5] plant, soil and biological specimen [6]. The main pluses of ICP method is that large amount of samples can be analyzed within a short period of time. The disadvantages include memory effect, mass fractionation and interference due to spectral overlapping [7-10].

Mass spectrometry technique involves the use of thermal ionization to generate ions. This can be operated in both positive and negative modes and is generally referred to as positive thermal ionization mass spectroscopy (PTIMS) and negative thermal ionization mass spectroscopy (NTIMS)[3]. PTIMS method consists of pretreatment stage that involves separation of boron in the sample and converts it to metaborate complex by addition of basic salt. The complex is then ionized to metaboratecation in form of $MBO_2^+$and sent to detector where mass to charge ratio is measured [11, 12]. In NTIMS, similar procedure is carried out but measurement is done in form of BO_2^- . It requires no addition of basic salt, less pretreatment and has high sensitivity [7, 13]. Both PTIMS and NTIMS however have problems of mass fractionation and spectra interferences but more pronounced in PTIMS [7, 14].

Ionometric approach involves conversion of boron in sample to tetrafluoroborate ion by treating the sample with hydrogen fluoride HF. The tetrafluoroborate ion is then quantified potentiometrically through a suitable tetrafluoroborate ion selective electrode [3, 9]. This method is susceptible to high degree of error when boron concentration in the sample is low due to decrease in sensitivity of the electrode. In addition, the tetrafluoroborate electrode has interference problem from anions such as nitrate, sulfate, and iodide which in turn affect its applicability [15].

Spectrophotometry is a non-mass spectrometry technique for boron determination in samples based on the use of specific reagents. It is subdivided in to two categories, the colorimetric and the fluorimetric. In colorimetric method, the reagents react with boron in solution to form colored boron complexes which is passed through a detector where the amount of light absorbed is measured at a wavelength equivalent to the color properties of the reagent used [3, 16]. The commonly used reagents in this regard are curcumin, carmine and azomethine-H at 550, 605 and 410nm wavelength respectively [16-

18]. The fluorimetric method involves formation of fluorescent compounds from reaction between boron and the reagents and fluorescence of the compounds is then measured in the detection unit. Chromotropic acid and Alizarin Red are the frequently used fluorimetric reagents [3, 9]. Azomethine-H is the most widely used spectrophotometric method owing to the fact that it is simple, fast, sensitive and has least interference with other chemical species [3, 9].

The Azomethine-H approach can be used for both batch and continuous mode of analysis but optimization of measurement condition has not been fully carried out.

The objective of this study is to establish the optimum conditions for boron determinationin irrigation water using the azomethine-H spectrophotometry technique.

II. Methodology

2.1 Materials and Equipment
All the reagents used in this study were of analytical grade supplied by Fisher Scientific, United Kingdom.

Two azomethine-H reagents were prepared.The first sample was made by dissolving 0.5g Azomethine-H and 1g of ascorbic acid in 50ml of distilled water and transferred to a plastic bottle. The second sample was made of same amount of azomethine-H without ascorbic acid in 50ml of distilled water in similar bottle.

Buffer solution was made by dissolving 50g of ammonium acetate in 100ml of distilled water followed by addition of 25ml of glacial acetic acid and 1.4g of EDTA disodium salt.

UV-Vis CECIL CE 1021, 1000 series spectrophotometer was calibrated according to the manufacturer's manual and used to determine absorbance at a particular wavelength with 10mm 100-Qs cell.

2.2 Sample preparation
Various boron solutions were prepared from boron standard solution of 1000ppm to mimic the concentration of boron in irrigation water. Three different sub-samples; 100, 20 and 10ppmB were prepared from the stock by pipeting 10, 2 and 1ml respectively and diluting with distilled water to make up 100ml each. Several boron solutions between 0.1-10ppm were prepared from the sub-samples and UV-Vis was used to record absorbance for establishment of boron calibration graph.

2.3 Sample treatment
Samples prepared for analysis were treated as follows: Known amount of buffer solution was added to 10ml of the sample. Then, followed by some drops of azomethine-H reagent in a plastic bottle and stored in a dark space for a certain period of time. Thereafter, the absorbance readings were taken from the UV-Vis spectrophotometer. Procedures 2.2 and 2.3 were carried out in triplicates.

2.3 Analytical Method Development
The azomethine reagent was made from azomethine-H and ascorbic. 0.5g of azomethine-H and 1g of ascorbic acid dissolved in 50ml distilled water which translates to 0.0216 and 0.1136M respectively. In order to investigate the effect of ascorbic acid in the reagent, two fresh solutions of 0.0216M azomethine-H were made, one with ascorbic and other without ascorbic acid at pH 5.24 and stored in a dark place at room temperature. After every 30 mins, the colour development in the reagents varied greatly. It was observed that ascorbic free reagent darkened at a faster rate while no change in colour was observed in the reagent with ascorbic acid. The same procedure was again followed and the pH adjusted to 2.0, 3.0, 6.0 and 8.0. Similar observations were noted. This indicates that the presence of ascorbic acid in the reagent prevented it from oxidation. The integrity therefore could be maintained throughout certain experimental period. The extent of this stability was further scrutinized. Another azomethine sample was prepared containing the same amount of ascorbic acid and stored in a plastic bottle. After every 15 mins, no noticeable change in colour was observed. This continued for about 20 hours and thereafter changes were noted. This indicates that azomethine reagent containing ascorbic acid can be used for a period up to 20 hours from the time of its preparation.

To further investigate the effect of ascorbic acid on the azomethine-H, absorption spectra of azomethine-H were examined. Two fresh samples were prepared, one with ascorbic and the other without ascorbic acid. 2.5ml of each sample were added separately to 10ml of distilled water which is equivalent to 4.32×10^{-3}M of azomethine-H and the scans were conducted at various pH and wavelength using distilled water as blank.

III. Discussion of Result
Plots of absorbance against wavelength were obtained for the two scenarios as shown in Figure 1 and 2 below. Similar trends were obtained from the plots which confirm that the presence of ascorbic acid in the reagent has no effect on the absorption spectra of azomethine-H. The plots also show shift in spectra with respect to pH. This may be due to the nature of ionized azomethine-H species present in the sample. This situation is more obvious at pH value of 7 and above. However, in the acidic medium that is, pH values between 2 to 6, the changes tend to diminish from 400 to 430nm wavelength. This therefore provides an idea of pH less sensitive region for the measurement. Since the principle of Azomethine-H method is based on formation of color complex with boron in the sample, another scan was conducted at different pH with fresh 10ml of sample containing 0.5ppm boron and 2.5ml of reagent (2.5ml of azomethine-H with ascorbic acid) was added. The reagent was used as blank. The plot obtained shows that azomethine-boron complex is also affected by the pH of the solution as shown in Figure 3 below. The absorbance of the complex tends to stabilize in the acidic region between wavelengths of 410 to 430nm, although there were differences in the spectra. Full stability in absorbance value was observed at pH of 5.28 starting from 410nm wave length. This reveals that measurement can be carried out between

wavelength of 410 and 430nm with proper control pH of the solution within 5.2-5.3. Wave length of 415nm was adopted for this experiment.

The above investigation has identified the need for proper control of solution pH in order to take measurement at 415nm. Adequate buffer solution is required to maintain the pH within the appropriate range. A buffer solution was then prepared by dissolving 50g of ammonium acetate in 100ml distilled water followed by addition of 25ml of glacial acetic acid. 1.4g of EDTA salt was added to avoid any interference from other ions during boron measurement stage. The solution was subjected to several tests. Two sets of distilled water with pH adjusted to 3.5 and 9.5 were treated as follows: 1ml of buffer solution was added to 10ml of each water sample followed by 4ml of azomethine reagent to make up total volume of 15ml. The pH values of resulting mixtures were found to be 5.33 and 5.37 respectively. The same procedure was repeated for 1.5, 2.0 and 2.5ml of buffer with corresponding azomethine volume of 3.5, 3 and 2.5 and the pH of final mixtures were 5.30, 5.26 and 5.24 for water sample at initial H value of 3.5 and 5.33, 5.30 and 5.26 for sample at pH 9.5. Boron solutions of 0.5ppm at different pH were treated in a similar manner with 2.5ml of buffer and 2.5ml azomethine. The pH of final solution is shown in Figure 4 below. The figure clearly indicated the effectiveness of the buffer solution in controlling the pH within the desired range. Thus, it is recommended that for every 10ml of sample, 2.5ml buffer and 2.5ml of azomethine reagent should be used. This procedure was adopted throughout the following investigations.
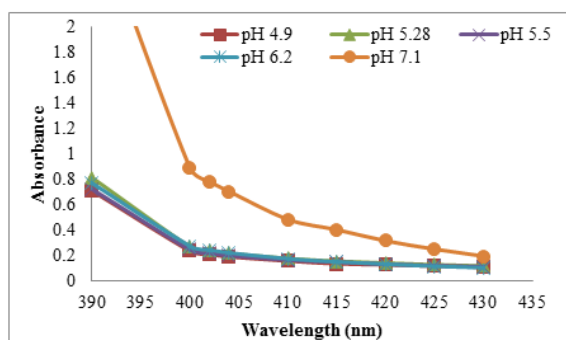

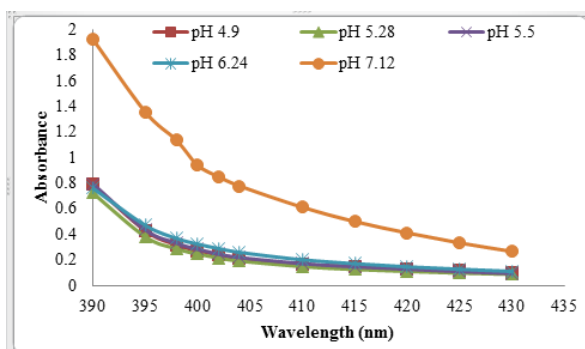**Figure 1**: Absorption spectra of 4.32x10-3M azomethine-H without ascorbic acid using distilled water as blank

Figure 2: Absorption spectra of 4.32x10-3M azomethine-H with 0.023M ascorbic acid using distilled water as blank
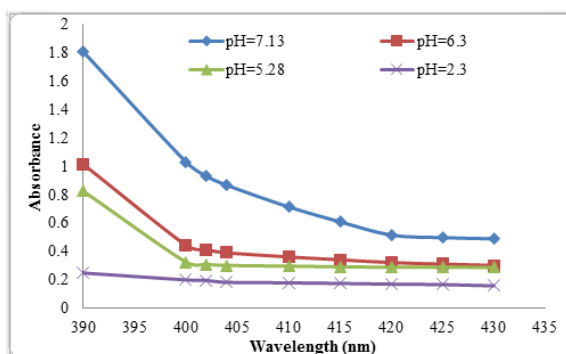

Figure 3: Absorption spectra of azomethine-boron complex using reagent blank

Generally, when azomethine-H reagent is added to sample buffered at particular pH, it quickly form hydrolysis product within certain period of time and after which, the product re-condenses to form Schiff base with concentration equivalent to the concentration of boron in the sample. Therefore, the time for full color development is necessary to identify the waiting period needed for the sample to be stored before measurement is taken. This situation was investigated with 0.5ppm boron solution and reagent blank under room temperature. The scans were performed against pure distilled water. The result as shown in Figure 5 indicates that the absorbance became maximum and constant after 40minutes. Consequently, the time required for full colour development is 40 min. All the samples treated using the recommended procedures are stored in a dark place at room temperature for 40minutes before absorbance readings were taken.

Boron calibration graph was constructed. Samples made from different boron standard solutions using the recommended procedure. Absorbance was measured against reagent blank after 40minutes. Plot of absorbance against boron concentration followed Beer's law from 0.1-3ppmB at 415nm. Eight point calibration as shown in Figure 6 indicates a very good linearity between absorbance and the boron standard solution with r^2 value of 0.9998. A residuals plot was also established as shown in Figure 7. From the chart, the residual values are randomly distributed between the positive and negative axis. This gives a further confirmation of straight fit to the data.
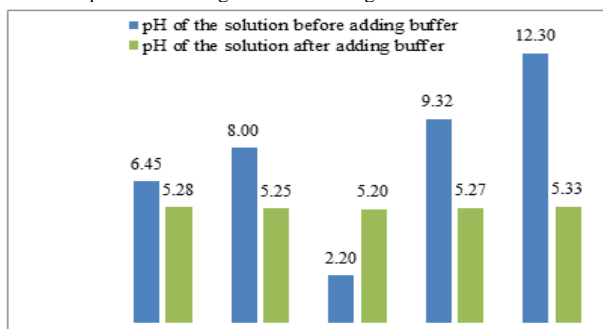
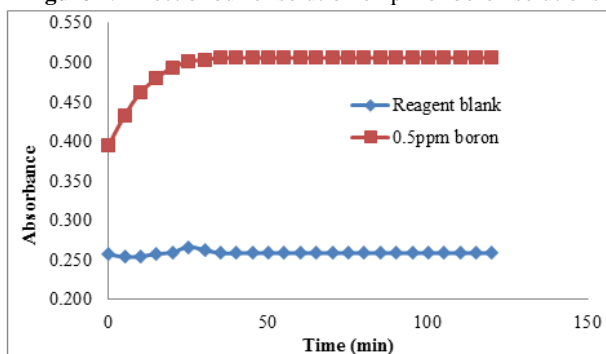**Figure 4**: Effect of buffer solution on pH of boron solutions

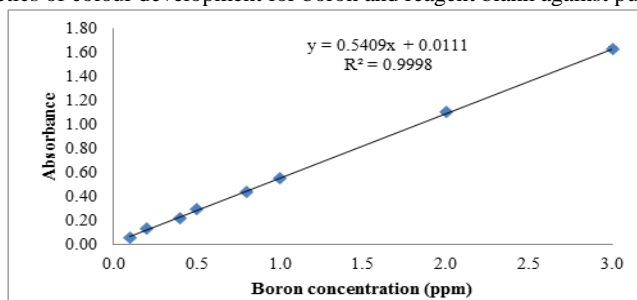**Figure 5:** Kinetics of colour development for boron and reagent blank against pure distilled water

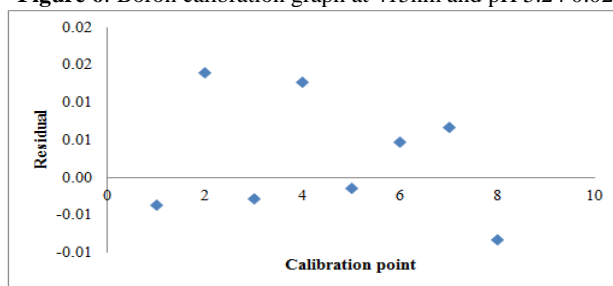**Figure 6**: Boron calibration graph at 415nm and pH 5.24 0.02

Figure 7: Chart of residuals from the regression Line for calibration points

IV. Analytical Method Validation

The analytical method used for the determination of boron in the water was validated by computing the error or uncertainty in the measurement. The uncertainty in the regression ($S_{y/x}$), slope (S_m) and intercept (S_c) were calculated using equation (1), (2) and (3) respectively.

$$S_{x/y} = \sqrt{\frac{\sum(y_i - y_{ic})^2}{n-2}} \ \text{---------------------------} (1)\,[19]$$

$$S_m = \frac{S_{x/y}}{\sqrt{\sum(x_i - x_{av})^2}} \ \text{------------------------} (2)\,[19]$$

$$S_c = S_{x/y} \times \sqrt{\frac{\sum x_i^2}{n \times \sum (x_i - x_{av})^2}} \quad - (3)\ [19]$$

Where y_i represent the value of measured absorbance and y_{ic} is the absorbance value calculated using the regression equation obtained. x_i and x_{av} represent the concentration and the average concentration.

The 95% confidence limit for slope and intercept are obtained from equation (4) and (5) each.

$$m \pm t \times S_m \quad - (4)\ [19]$$

$$c \pm t \times S_c \quad - (5)\ [19]$$

Limit of detection (LOD) represents the minimum value of concentration of analyte that can be measured by the instrument. This is given in terms of uncertainty of the regression and the intercept.

$$Abs_{LOD} = c + 3 \times S_{y/x} \quad - (6)\ [19]$$

Table 1 below gives the estimated statistics and limit of detection at 95% confidence level

Table 1: Values of the parameters determined

Parameter	Value
n	8.00000
m	0.54090
c	0.01110
X_{av}	1.00000
Y_{av}	0.55200
$S_{y/x}$	0.00926
S_m	0.00345
S_c	0.00474
LOD (Abs, ppm)	0.03889, 0.05137
t-value(95% Confidence level)	2.44691

V.   Conclusion

Analytical method has been developed for quantification of trace amount of boron in water using azomethine-H. The procedure was further optimized. It was found that azomethine-H reagent can be used for analysis for a period up to 20 hours from the time of its preparation. This will go a long way in reducing the cost of analysis and time. The time required for full color development was found to be 40 min at room temperature. Optimum pH of 5.24 ± 0.02 for the measurement at wavelength of 415nm was identified. This method provides wide linearity up to 3ppmB with limit of detection of 0.0514ppm within 95% confidence level. The proposed analytical method demonstrates good sensitivity, accuracy and highly selective for determination of boron in aqueous solution.

Acknowledgements

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