Analysis Methods Verification of Boron in River Water Using the UV-Vis Spectrophotometer with Curcumin Complex as Alternative Practical Educations

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ABSTRACT: Boron is one of the industrial wastes included in the hazardous and toxic materials category. The purpose of this study was to determine river water sample levels and determine the value of linearity, RSD, and% recovery. The method used is under APHA - AWWA 4500 B. Some boron complexing compounds include curcumin in acetic acid, carminic acid, and quinalizarin, but in this study, curcumin complex are used because their sources in Indonesia are abundant. Curcumin gives a red complex color as an indication of the presence of boron in the sample. This phenomenon makes the learning process through practicum very interesting. Students can see the color change directly from orange to red. Students taught to produce reliable data and understand the importance of the chemist and analyst profession for the community through the practice of verification and validation methods, and the determination of the value of boron. Based on this study, it concluded that the Boron content in river water samples is 0.4766 mg / L. These results obtained from the straight-line equation that is y = 0.3446x - 0.0119 with R2 of 0.9976. The results of the RSD analysis are 0.028%, which states that the value is in the Horwitz TABLE range. Therefore, it can be accepted. Besides, the% Recovery is 86%; this value meets the analysis standard and is acceptable because it is in the range of 85% -115%. Finally, the measured boron levels in river water samples are still below the quality standard limits of the Republic of Indonesia Government Regulation Number 82 of 2001 concerning water quality treatment and water pollution control with a value of boron levels less than 1 mg/L. The boron content in a sample of river water in the Semarang area is still safe.

Keywords: boron, practical educations, analytical chemistry, linearity, rsd, % recovery

INTRODUCTION

In Indonesia and several other developing countries, B3 waste is still commonly found as dumped waste in rivers. The lack of public and industrial awareness and the lack of supervision from the government also to the non-strict regulations causes that there is still a lot of waste dumped in the river [1].

River pollution needs to early identify because, in some river areas, it is still a source for various human activities. Generally, river water is even used for washing, bathing, drinking water sources, and irrigating rice fields. According to Diana Hendrawan, "rivers in Indonesia are widely used for human needs such as water reservoirs, transportation facilities, irrigating rice fields, livestock needs, industrial needs, housing, catchment areas, flood control, water availability, irrigation, fishing grounds and also as recreational areas [2].

Boron is one of the industrial wastes included in the hazardous and toxic materials category. The Indonesian government calls it B3 waste. In Indonesia, Boron is a B3 waste regulated in the “Government Regulation of the Republic of Indonesia Number 82 of 2001 concerning water quality treatment and water pollution control”. The main watersheds tend to have a higher pollution potential than rivers in the periphery. Therefore, in this study, boron analysis was carried out on river water.

Boron is widely distributed in the environment from natural or anthropogenic sources and can be found mainly in the form of boric acid or boric salt [3]. Boron accumulation in river water can be toxic to plants such as leaf edges and necrosis, yellowing spots, reduction of the division of root cells, dwarf, then

followed by weakening of photosynthesis, which can lead to plant death. Humans and animals can also be affected by boron, although the mechanism of its toxicity is unclear. Side effects of boron can cause problems in the heart, coronary, nervous, and reproductive systems. Also, changes in blood composition, retardation of children can occur [4].

Considering that boron accumulation can be hazardous, every laboratory that conducts boron analysis must ensure that the method of determining the value of boron contained in river water is valid and accurate. UV-Vis spectrophotometry method is often used in the determination of boron and done by several types of complexing, including curcumin in acetic acid, carminic acid, and quinalizarin [5]. Curcumin is a complexing compound that is often used in boron analysis because the source of curcumin in Indonesia is very abundant [6-10]. Curcumin and boron will produce rosocyanin-colored complexes [11]. Based on this review, this study aims to measure boron levels in one of the river waters in Semarang and ensure the procedures used can provide reliable data [12]. It is necessary to verify the method of determining boron with curcumin to prove that the process meets the requirements for its use. Test parameters in the verification of this method include linearity, precision, and accuration. This article ensures that this method can be used with a high degree of confidence so that the data obtained truly represents the amount of compound present in the sample.

In addition to river water samples, boron analysis is usually carried out on food samples to determine levels of boric acid. Given the importance of boron analysis and the analytical skills of graduates with a chemical background, boron analysis is highly recommended to introduce to students. This method can be applied to an analytical chemistry practicum in the environment of diplomas, chemistry scholars, or chemistry education. This journal is great for those who are looking for a simple and inexpensive practical analysis method. The materials used in this analysis are also easily available, especially in the Indonesian environment.

METHODS

Class delivery method

This lecture is designed to deliver in a practical class at a chemical laboratory with a duration of approximately 2-3 hours. Within that duration, practical work and a brief explanation of chemical reactions as well as the way statistical calculations are possible to convey. Although a detailed calculation of the results of student work is finished outside hours of practice.

Materials and tools

The materials used in this study are curcumin, oxalic acid, concentrated HCl, 96% alcohol, tissue, distilled water, and a sample of river water from the Semarang area.

The instruments used in this study were UV-Vis spectrophotometer, analytical balance, water bath, porcelain cup, 1 mL volume pipette, 10 mL pipette, glass stirrer, 200 mL measuring flask; 100 mL; 50 mL; 25 mL, cuvette, funnel and beaker glass.

Preparation for Curcumin Reagents

10.0341-gram oxalic acid and 0.0819-gram curcumin were dissolved using 96% alcohol and added 8.4 mL concentrated HCl to a 200 mL volumetric flask.

Preparation of Boron Standard Solution

Prepare a 1000 ppm standard boron solution and subsequently make a standard solution with a concentration of 0.2; 0.4; 0.6; 0.8; 1,2; 2; and 10 ppm.

Preparation of the Standard Curve of the Boron-Curcumin complex

1 mL of each standard boron pipette and 4 ml of curcumin solution added to the vaporizer cup. The mixture was then evaporated in a water bath at 55 °C and left for less than 80 minutes to dry. Followed by cooling at room temperature and dissolving with 96% alcohol into a 25 mL volumetric flask. Each sample was ready to be tested using UV-Vis spectrophotometry at a wavelength of 540 nm.

River water sample analysis

1 mL of each river water sample was pipetted, and 4 mL of curcumin added to the vaporizer cup. Further samples were treated exactly like the standard until tested using UV-Vis spectrophotometry with the absorbance of 540 nm.

Manufacture and Testing of Spike Solutions

1 mL standard solution of 10 ppm pipetted, and sample solution added to the marking limit of 25 mL measuring flask. This solution is then homogenized. The next step is 1 mL of spike solution and 4 mL of curcumin added to the vaporizer cup. Further samples were treated exactly like the standard until tested using UV-Vis spectrophotometry with the absorbance of 540 nm.

RESULT AND DISCUSSION

Boron analysis is usually done in various analysis laboratories of the government and private companies, especially in the Ministry of Health, the Environment, and the Republic of Indonesia Food and Drug Supervisory Agency (BPOM). The analysis process usually refers to the analysis standards adopted from national or international standardization institutions. Therefore, it is essential for students to familiar with the standard methods used in various departments. It will help chemistry graduates to adapt to the work environment quickly. In addition to the analysis procedure, the validation method is also critical to introduce to students. Apart from the skill to determining the value of boron contained in a sample, a chemist must be capable of validating the method. The reliability of data from the results of the analysis will only be achieved if the procedure is valid and delivered by qualified analyst skills. Therefore, practicum Analysis Methods Verification of Boron in River Water Using the UV-Vis Spectrophotometer with Curcumin Complex can be an excellent alternative to give to students.

This analysis aims to determine the levels of Boron in river water samples and determine the value of% Recovery, precision, and linearity of determining the levels of Boron in river water samples with UV-Vis spectrophotometry. The method used in boron analysis is the curcumin method with the standard APHA-AWWA 4500 B. Research on boron analysis using the curcumin method involves making a standard boron curve, the process of analyzing samples with the curcumin method using UV-Vis spectrophotometry and making a spike solution to determine the% Recovery value.

Electromagnetic radiation from UV-Vis Spectrophotometry can interact with chemical species. The absorbed energy can excite electrons from the ground state to a higher state [13]. Energy changes are unique to each compound so that this energy is measured for sample analysis purposes. Measurements using UV-Vis spectrophotometry must be performed on colored analytes. Boron's solution is colorless. It is a problem because the solution that can be analyzed using UV-Vis spectrophotometry must have a chromophore group marked with color. Therefore, in this analysis, boron is reacted with curcumin. In addition to curcumin, other complexes can also be applied to indicate the presence of boron, but for educational purposes, curcumin is more recommended because it is easy to obtain and provides clear and attractive color changes. It will make the learning process with practical classes more fun for students.

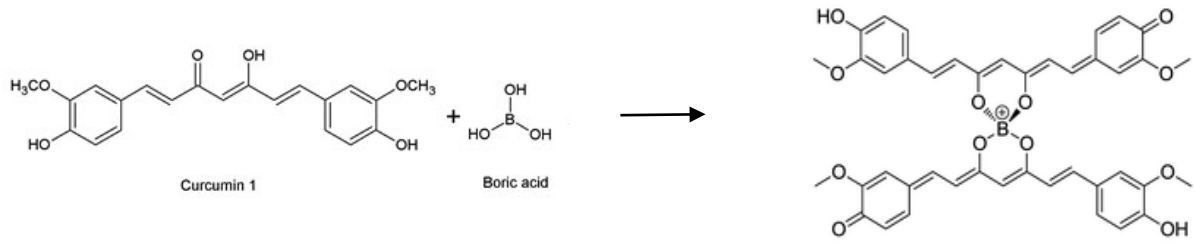

FIGURE 1. Mechanisms for boron and curcumin reactions [14,15]

Complex reactions that occur in boron and curcumin are presented in **FIGURE 1**. Curcumin has a maximum wavelength of 430 nm. At this maximum wavelength, the light will be absorbed and reflected in yellow. Curcumin then reacts with boron to form a complex [16]. When this complex occurs, a wavelength shift occurs from 430 to 540 nm [17], where all the light will be absorbed and reflected in red (rosocyanin) [18]. The feasibility of the boron analysis method with the curcumin complex is proven by the linearity test, precision, and accuracy test.

Linearity

Linearity is the ability of analytical work to produce rational responses that are direct and proportionate to the concentration of the analyte in the test sample [19]. The linearity test of a solution qualifies if the

relation coefficient approaches 1 [20]. Linearity tests are done by a series of standard solutions consisting of a minimum of four different concentrations ranging from 50-150% of the analyte content in the sample [21].

The linearity parameters used are the correlation coefficient (r) and the coefficient of determination. The coefficient of determination is the ratio of variation, which is explained against the overall variety and is marked with R2. A coefficient correlation is a measure of a linear relationship between two data sets and is indicated by r. The equation for linear regression is y = bx + a (b is a slope, a is the intercept, x is the concentration of the analyte, and y is the instrument response). The ideal linear relationship is the value of a = 0, and r = +1 or -1 is a relationship that perfectly depends on the direction of the line. A positive sign (+) indicates a positive correlation shown by the direction of the slash to the right, while a negative sign (-) indicates a negative correlation marked by the direction of the sloping line to the left. An excellent method in analysis has standard series linearity with the coefficient of determination (R^2) minimum 0.99 and the correlation coefficient ≥ 0.995.

Determination of linearity was done by measuring seven standard solutions of serial concentrations of 0.2; 0.4; 0.6; 0.8; 1,2; and 2 ppm. The absorbance of this solution was measured at a wavelength of 540 nm. Measurement data for absorbance of standard solutions are shown in **TABLE 1.**

TABLE 1. Absorbance data of standard boron solutions

Standard Concentration (ppm)	Absorption
0.0000	0.0001
0.2000	0.0585
0.4000	0.1142
0.6000	0.2068
0.8000	0.2500
1.2000	0.3923
2.0000	0.6873

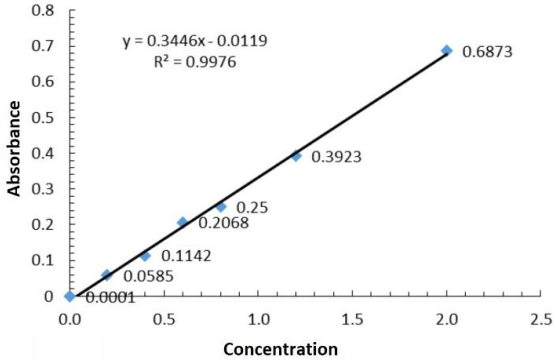

FIGURE 2. Standard curve of the boron-curcumin complex

Regression curves are made from these data to determine the concentration of the sample, and in the future, its called a calibration curve. The calibration curve is shown in **FIGURE 2.** The calibration curve has a slope (B) value of 0.3446 and an intercept value (A) of (-0.0119). The slope and intercept data formed a straight-line equation, y = 0.3446x-0.0119. Based on the data above, the standard concentration is linearly proportional to the absorbance value. Excellent linearity is characterized by a correlation coefficient close to 1. Absorbance measurement of Boron standard solution using UV-Vis spectrophotometry at a wavelength of 540 nm has a high enough linearity. It is proved by the value of the correlation coefficient (R^2) obtained from the curve is 0.9976. It fulfills the minimum correlation required for Boron content analysis (minimum r value is 0.995). Therefore, the results of the preparation of standard solutions have a pretty good level of accuracy. The regression data obtained is already close to the actual data (a small enough difference with the real data).

Precision

Precision is a value that indicates the degree of agreement between individual test results. It is measured by the spread of individual results from the average. This procedure must be applied repeatedly to samples taken from a homogeneous mixture. The precision evaluation of data analysis is completed by calculating the standard deviation. The standard deviation is obtained by measuring the distribution of experimental data and giving a good indication of how close the data is to each other [22]. The calculation of standard deviation is determined by **Equation 1.**

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \quad \text{.....} \quad \text{Equation 1. Standard deviation}$$

$$RSD = \frac{SD}{\bar{x}} \text{ x } 100\% \quad \text{.....} \quad \text{Equation 2. Relative standard deviation}$$

A precision test is performed to determine the accuracy or suitability of the results with the actual values. Precision is determined based on the analysis of reliability, with the provisions of the same analyst, laboratory, and tool, as well as adjacent time intervals. It is required to determine the suitability of the method with the test sample and the testing process. The result of the precision determination is obtained by measuring the absorbance of the sample solution by Uv-vis spectrophotometry. Absorbance value is then converted to a concentration value. This data can be seen in **TABLE 2**.

TABLE 2. Sample precision measurement data

No.	Name	Absorbance	Concentration (ppm)
1	Sample 1	0.1600	0.4985
2	Sample 2	0.1480	0.4744
3	Sample 3	0.1507	0.4638
4	Sample 4	0.1474	0.4715
5	Sample 5	0.1571	0.4621
6	Sample 6	0.1519	0.4903
7	Sample 7	0.1516	0.4753
	Average	**0.4766**	
	SD	**0.013**	
	RSD	**0.028%**	
	%CV*0.67	**11.90%**	

The data obtained was analyzed by RSD (Relative Standard Deviation). RSD value is a Quality Control Test Result to determine the accuracy (precision) of the analysis results. RSD value of this calculation is 0.028%. RSD values are matched with Horwitz TABLEs. According to Horwitz's TABLE, concentrations in the range of 0.4766 ppm should not have an RSD value of more than 11.90%. Therefore, the RSD value of 0.028% meets the analysis standard. It explains that the data has excellent precision, gives a small standard deviation and low bias.

The measured value of boron levels in river water samples is 0.4766 mg/L. Based on Republic of Indonesia Government Regulation Number 82 the Year 2001 regarding water quality treatment and water pollution control, the maximum boron content for river water is 1 mg/L. Therefore, the measured boron content in the sample is still below the specified standard quality range. If the boron content is above the usual quality standard, it can endanger the environment. The discharge of industrial waste may cause high levels of boron into the river water.

Accuracy

Accuracy is one of the verification parameters of the analytical method that illustrates the closeness of the measurement results with the actual value. One way to determine the accuracy parameters is the spike or percent recovery technique (% recovery). The spike technique aims to evaluate or see the effect of the sample matrix on the analyte from a standard solution. This technique is completed by adding a standard solution with a certain amount in the sample solution. As for the spike requirements, the sample must have a concentration, the spike is done twice or three times the average concentration of the sample, and the result of the concentration of the spike must not be higher than the highest standard concentration.

TABLE 3. Accuration measurement data

	Absorbance	Concentration (ppm)
Sample	0.0378	0.1441
Spike	-	0.4000
Sample + spike	0.1564	0.4881
% recovery	86%	
Acceptance	85%<5R,115%	
Conclussion	Accuration accepted	

In this analysis, the spike solution was made with 1 ml of standard boron solution and diluted with a sample solution of up to 25 ml, then analyzed by UV-Vis spectrophotometry. The accuracy of the results can be seen in **TABLE 3**. Based on the APHA-AWWA method, the% recovery received ranges from 85%

to 115%. This value can be reviewed by the implementation of continuous improvement policies applied in the laboratory. From the data in **TABLE 3**, the% Recovery value is 86%. This value meets the analysis standard and is acceptable because its value is in the range of 85% - 115%.

Conducting verification and validation methods will provide the perception that the data they produce can be trusted while the process of determining the value of boron content in samples and comparing with existing regulations provides experience in deciding whether a sample is acceptable / not for consumption. It is a unique experience that will be attached to students and gives them confidence that the chemist or analyst is an essential profession in the community.

CONCLUSION

Based on this study, it concluded that the curcumin gives a red complex color as an indication of the presence of boron in the sample. It makes the learning process through practicum very interesting. Students can see firsthand the color change from orange to red. Through the practice of verification and validation of methods, as well as determining the value of boron, students are also taught to produce reliable data and even understand the importance of the chemistry profession for the community. Boron content in river water samples is 0.4766 mg/L. These results obtained from the straight-line equation that is y = 0.3446x - 0.0119, with R2 of 0.9976. The results of the analysis of the RSD value of 0.028% which states that the value is in the Horwitz TABLE range so that it can be accepted, while the% Recovery value of 86%, this value meets the analysis standard and is acceptable because the value is in the range of 85% -115%. Finally, the measured boron levels in river water samples are still below the quality standard limits of the Republic of Indonesia Government Regulation Number 82 of 2001 concerning water quality treatment and water pollution control with a value of boron levels less than 1 mg/L. The boron content in a sample of river water in the Semarang area is still safe.

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