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Critical Quality Control on Determination of Boron Using ICP-OES with Gravimetric Method

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ABSTRACT

Critical quality control on the determination of boron using ICP-EOS with gravimetric method is carried out. This study was conducted to examine the critical aspects which include linearity, LOD, LOQ, precision, and accuracy. Based on the results of the study showed that the determination of boron with the ICP-OES method was following the critical aspects of quality control test results. The linearity of the calibration curve with a concentration range of 0 - 10 mg/L has linearity with a correlation coefficient of 0.9998 and a determination coefficient of 0.9996. The standard solution calibration curve follows the linear regression equation y = 2567.5 x + 23.043. This method has a LOD of 1.24 mg/L and a LOQ of 4.13 mg/L. The ICP-OES method has high precision and accuracy at low, medium, and high concentration levels. The testing precision of low, medium and high concentration levels is 0.44, 0.54, and 0.14%. The accuracy obtained for the three concentration levels was 98.03, 95.05, and 98.61%. Based on the ANOVA test, it was shown that the precision and accuracy at all concentration levels were not significantly different.

1. INTRODUCTION

Boron is an element present in geothermal fluids. Boron content in geothermal fluids is used for geochemical evaluation. The boron content is used to evaluate fluid flow to the surface [1]. Fluid flow can cause a decrease in the concentration of solutes in the rock through which hot water flows [1], [2]. The boron content can be used to determine the geothermal source zone [1]. The geothermal wells are characterized by a wide range of Cl/B ratios [1]–[3]. Therefore, the boron content in geothermal fluids must be continuously evaluated.

The boron ccontent in geotermal fluids is found at a low concentration level [1]. These tests require methods that can detect at low concentrations with high precision and accuracy. The determination of boron can be carried out by the method of atomic absorption spectroscopy (AAS) [4]–[6]; UV-Vis spectrophotometer [4], [7], [8]; inductively coupled plasma–optical emission spectrometry (ICP-OES) [4], [9], [10]; inductively coupled plasma mass spectrometry (ICP-MS) [4], [9], [10], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [11], [12] and microwave plasma atomic emission spectrometry (MP-AES) [6].

The ICP-OES method is more widely used for the determination of total boron at low concentrations. The method is simpler, sensitive, and practical, has good selectivity, good accuracy,

and a linearity range of 1-1000 µg/L [13]. One of the problems in the determination of boron is the possibility of contamination with glassware made of borosilicate [9]. This problem has an impact on the accuracy of boron testing in geothermal fluids that are at low concentration levels. Therefore, all volumetric measuring equipment must use plastic materials, such as polyethylene. However, calibrated plastic volumetric measuring instruments are not always available in the laboratory.

The preparation of standard solutions is a critical aspect of the determination of boron. Preparation of standard solutions requires dilution and requires appropriate volumetric equipment. The limitations of this measuring pipette and volumetric flask can be modified by gravimetric techniques. The standard solution was prepared by weighing. This study was conducted to study the critical aspects of the modification of the standard solution preparation method gravimetrically at low, medium, and high concentration levels. The results of this study can be used as recommendations for the development of routine procedures for determining boron in geothermal fluids at low concentration levels.

2. MATERIALS AND METHODS

2.1. Materials

The materials used in this study included type I ultrapure distilled water and 25% nitric acid solution. The standard solution used is a standard solution of 1000 ± 0.2 mg/L boron material in water traceable to NIST from Loba Chemical Pvt. Ltd. The standard series was prepared by diluting a standard solution of 1000 ppm. The standard series was prepared using 3.25% HNO_3 solvent in ultrapure distilled water type 1. Standards are made using equipment made of HDPE plastic. The solution was taken by weighing using the gravimetric method. The use of this plastic is done to avoid contamination of borosilicate glass.

2.2. Determination of Linearity, Limit of Detection, and Limit of Quantification

Determination of linearity was carried out by measuring the intensity of the boron standard series solution using ICP-OES. The measurement results made a standard solution calibration curve to get the slope, intercept, and correlation coefficient values. The detection limit and quantification limit values are calculated from the standard deviation of the residual from the measurement of the intensity of the boron standard series solution

2.3. Determination of Precision and Accuracy

Determination of precision and accuracy using standard reference materials with concentrations of 1.5, 5, and 7.5 mg/L.

3. RESULTS AND DISCUSSIONS

3.1. Determination of Linearity, Limit of Detection, and Limit of Quantification

The linearity of the standard solution calibration curve is shown in Figure 1. Figure 1 shows that the calibration curve of the standard boron solution follows the linear regression equation $y = 2567.5 x + 23.043$. The calibration curve made gravimetrically by weighing shows the sensitivity of the instrument used to an element being analyzed. The slope value in the linear regression equation shows a high ICP-OES sensitivity. The comparisons of the sensitivity of the linear regression equation with previous studies are presented in Table 2. The intercept on the calibration curve shows the possibility of a nuisance that can make the curve non-linear, the smaller the intercept value, the smaller the possibility of a nuisance that can make the calibration curve non-linear. Based on the linear regression equation, it shows that the intercept value in this study is lower than the research conducted by [11], [14], [15] as presented in Table 2.

Determination of linearity was conducted to determine the correlation between the analyte concentration tested with the instrument from ICP-OES giving an intensity response using a linear concentration. Based on the study that has been carried out, the value of the coefficient of correlation (R) and the coefficient of determination (R^2) on the standard calibration curve for boron are 0.9998

and 0.9996. The gravimetric preparation of standard solutions gives good linearity to the calibration curve of boron standard solutions. Based on the test results indicate that the value of $R \geq 0.999$ indicates that the linear regression equation according to the acceptance criteria for the linear regression test, namely $R^2 \geq 0.950$. The value of R^2 shows a linear relationship between the measured detector signal and the number of elements in the standard solution. This linearity shows that this method has good linearity as previous studies using the ICP-OES, ICP-AES, and MP-AES methods are presented in Table 2.

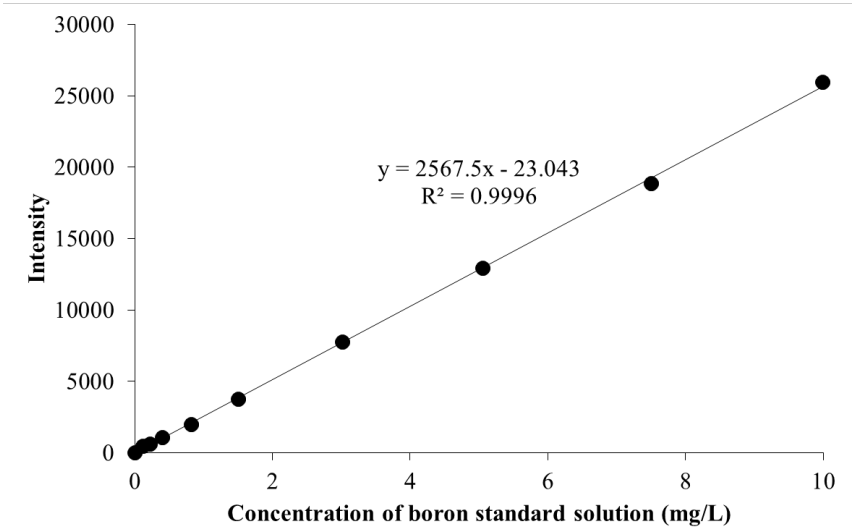

Figure 1. Calibration curve of boron using ICP-OES with gravimetric method

TABLE I. Determination of LOD and LOQ of boron using ICP-OES with gravimetric method

Concentration, mg/L (x)	Intensity (y)	y_i	$y_i - y$	$(y_i - y)^2$
0.00	0	-23.04	-23.04	530.98
0.12	1028.87	281.84	-747.02	558042.94
0.23	1187.66	557.07	-630.59	397638.46
0.41	1631.53	1021.16	-610.37	372557.13
0.82	2574.60	2087.77	-486.83	237000.74
1.51	4361.80	3844.36	-517.44	267739.54
3.02	8356.03	7731.56	-624.47	389960.68
5.05	13485.65	12951.03	-534.62	285818.77
7.50	19433.38	19228.07	-205.31	42154.10
9.99	26532.94	25628.66	-904.28	817716.29
Σ (yi-y)²				3369159.63
Sy/x				1059.74
LOD				1.24 mg/L
LOQ				4.13 mg/L

Determination of boron using ICP-OES with gravimetric method has good results. The emission spectrum produced from each metal in the other tests is characteristic because in general the atomic emission measurement method is specific and has high sensitivity. Inductively coupled plasma optical emission spectrometry can read wavelength differences up to 0.1 nm. This shows good sensitivity results, therefore, ICP-OES does not experience much spectral interference as in AAS. The ICP-OES instrument is also carried out simultaneously, with only one measurement, the desired metal content can be directly measured. This is indicated by the specificity of the emission spectrum of each program combined with a particular optical system so that each metal whose optimum wavelength has been selected can be identified sequentially.

The presence of boron contamination from volumetric equipment made of borosilicate will give sensitivity to the test. In the measurement of low concentration levels, it reduces the accuracy of the test. Moreover, this method has a low limit of detection limit and limit of quantification. The limit of detection and limit of quantification are presented in Table 1. The limit of detection for boron determination is 1.24 mg/L. This detection limit is used to determine the smallest boron concentration that can be measured by the ICP-EOS. Boron with a concentration of 1.24 mg/L can be detected with more significant results than the blank. The quantification limit obtained was 4.13 mg/L. This limit of quantitation can be used to ensure the lowest boron concentration that can still be measured with good precision and accuracy.

TABLE II. The comparison of linearity, LOD, and LOQ for the determination of boron

Methods	Range concentration (mg/L)	Linear regression equation	Coefficient correlation	LOD	LOQ	Ref.
AAS				1 mg/L		[6]
				0.5 mg/L		[16]
	0.0025 – 0.600			0.75 µg/L		[5]
UV-Vis	0 – 2	y = 0.3446x – 0.0119	0.9976			has
Spectrophot	0 – 7	y = 0.1081x + 0.024	0.9995			[8]
ometry	0 – 1.6	y = 0.5409 x + 0.0111	0.9998			[17]
ICP-MS	0 – 1.2			0.072 mg/L	0.012 mg/L	[10]
				0.010 µg/g		[18]
ICP-OES	0 – 1.2			0.012 mg/L	0.02 mg/L	[10]
				5.0 µg/g		[18]
	0 – 2.0	y = 9642 x + 16.26	0.999	0.001 mg/L		[6]
		y=6793x + 286.62	0.9995			[14]
	0 – 10	y = 1251x – 78.46	1			[19]
	0 – 1			20.0 µg/L	100.0 µg/L	[13]
	0.25 – 8.00	y = 7683 x + 1332	0.992	2 µg/g		[15]
ICP-AES	1 – 25	y = 53417 x + 5390	0.9999	0.10 mg/L	0.50 mg/L	[11]
	1 – 25	y = 19771 x + 496	0.9999	0.10 mg/L	0.40 mg/L	[11]
	1 – 25	y = 5274 x + 161	0.9999	0.15 mg/L	0.50 mg/L	[11]
MP-AES	0 – 2.0	y = 6962 x + 10.63	0.999	0.001 mg/L		[6]

3.2. Determination of Precision

The results of the determination of precision are presented in Table 3. The data in Table 3 shows that the gravimetric solution preparation method with 3 concentration variations gave good precision with % RSD less than 2% and 2/3 CV Horwitz. The ANOVA test on precision measurements on three concentration variations with degrees of freedom of 9 and confidence interval of 95% is presented in Table 5. Based on the results of the ANOVA test with df = 9 and confidence interval level of 95 %, it shows that the calculated $F_{value} < F_{crit}$. The results of the ANOVA test show that the calculated F value (F_{calc} = 0.2075) < critical F value (F_{crit} = 3.0204). The results of the ANOVA test indicate that the measurement of boron at a concentration of 1.5; 5; and 7.5 mg/L give a standard deviation that was not significantly different. It means, the precision at measurement with a concentration of 1.5; 5; and 7.5 mg/L did not give a significant difference. This value indicates that the result standard deviation is not significantly different so that the precision of the three concentration variations can be accepted [20].

Based on the test results showed that the determination of boron with the gravimetric method in low, medium, and high concentrations give high precision. This precision value can be compared with several previous studies presented in Table 7. Based on the %RSD value, it shows that the precision obtained is higher than the AAS [5], [16]; ICP-MS [10]; ICP-OES [6], [10]; ICP-AES [11]; and MP-AES [6] methods. Comparing precision with its acceptance requirements is a critical aspect in ensuring quality control of boron testing with ICP-OES.

TABLE III. Determination of precision at 3 concentration levels of boron using ICP-OES with gravimetric method

Replications	Concentration of boron (mg/L)		
	1.5	5.0	7.5
1	1.54	5.25	5.23
2	1.55	5.18	5.40
3	1.55	5.21	7.98
4	1.53	5.23	7.65
5	1.55	5.20	7.58
6	1.54	5.23	7.73
7	1.55	5.20	7.76
8	1.56	5.25	7.74
9	1.55	5.17	7.71
10	1.55	5.25	7.75
Average	1.54	5.21	7.25
Standard deviation	0.01	003	1.03
% RSD	0.50	0.56	0.14
CV Horwitz	14.49	12.34	11.83
2/3 CV Horwitz	9.79	8.27	7.89

TABLE IV**.** The ANOVA test on the determination of precision using ICP-OES with gravimetric method

Source of Variation	Sum of squares (SS)	Degrees of freedom (df)	Mean square (MS)	F	P_{value}	F_{crit}
Between Groups	4.7572	9	0.5286	0.2075	0.9866	3.0204
Within Groups	25.4739	10	2.5474			
Total	30.2311	19				

3.3. Determination of Accuracy

The results of the determination of accuracy are presented in Table 5. The data in Table 5 shows that the average accuracy of standard boron measurements is in the range of 85 - 115%. The ANOVA test on accuracy measurements on three concentration variations with degrees of freedom of 7 and confidence interval of 95% is presented in Table 5. Based on the results of ANOVA test with df = 9 and interval confidence level of 95 %, it shows that the calculated $F_{value} < F_{crit}$. The results of the ANOVA test show that the calculated F value ($F_{calc} = 0.8868$) < critical F value ($F_{crit} = 2.6572$). The results of ANOVA test indicate that the accuracy measurement shows that there is no significant difference in the mean value of % trueness at concentration of 1.5; 5; and 7.5 mg/L.

The ICP-OES with the gravimetric method has good accuracy for low, medium, and high measurement levels. Based on the data in Table 6 shows that the ICP-OES method has a high accuracy [10], [13] as the AAS [5]; UV-Vis spectrophotometry [8]; and ICP-MS [10]. Based on the precision values obtained and the previous research data presented in Table 6 and the acceptability

requirements of the accuracy range, it is a critical aspect in reviewing the selection of boron analysis methods with ICP-OES.

TABLE V. Determination of accuracy at 3 concentration levels of boron using ICP-OES with gravimetric method.

Replications	Trueness at standard concentration variations (%)		
	1.5	5.0	7.5
1	102.87	103.09	106.43
2	101.41	103.59	102.08
3	102.97	102.94	101.08
4	102.37	103.49	103.14
5	102.66	102.90	103.54
6	103.31	103.85	103.24
7	102.73	102.34	102.87
8	102.63	103.92	96.02
Average	102.62	103.26	103.20
%SBR	0.55	0.52	1.48

TABLE VI. The ANOVA test on the determination of accuracy using ICP-OES with gravimetric method

Source of Variation	Sum of squares (SS)	Degrees of freedom (df)	Mean squarP-value	F	P_{value}	F_{crit}
Between Groups	19.4628	7	2.7804	0.8868	0.5387	2.6572
Within Groups	50.1668	16	3.1354			
Total	69.6296	23				

TABLE VII. The comparison of precision and accuracy for the determination of boron

Methods	Sample	Sample preparation	Precision		Accuracy	Ref.
			SD	%RSD		
AAS	Plant	Digestion		4.4		[16]
	Beverage and dairy products	Cloud point extraction		1.9-2.3	99–102	[5]
UV-Vis Spectrophotometry with curcumin	River water		0.013	0.028	86	[7]
	Food product	Distillation			96.09-104.62	[8]
ICP-MS	Halite	Under salinity	0.012	2.8	97.5 – 102.34	[10]
	Water treatment process	Ultrafiltration	0.004		80 - 120	[9]
ICP-EOS	Halite	Under salinity	0.002	3.6	98.88 – 102	[10]
Bio sludge	Microwave-assisted	Microwave assisted acid digestion system		0.4 - 1.8		[6]
ICP-EOS	Water powdered food	alkaline media			99.80	[13] [15]
ICP-AES	Fertilizers	Digestion with acid		1,7-23,4		Bio sludge

4. CONCLUSIONS

Based on the results of the study showed that the determination of boron using ICP-OES with gravimetric method followed the critical aspects of quality control test results. The linearity of the calibration curve with a concentration range of 0 - 10 mg/L has a linearity with a correlation coefficient of 0.9998 and a determination coefficient of 0.9996. The standard solution calibration curve follows the linear regression equation y = 2567.5 x + 23.043. Based on the slope value obtained, it shows that the boron test with ICP-OES has good sensitivity with a relatively high slope. The intercept value obtained is much lower than the slope value, so this method can be used to minimize disturbances in the analyte response. The method has the limit of detection of 24 mg/L and the limit of quantification of 4.13 mg/L. This quantification limit can be used to ensure the lowest boron concentration that can still be measured with good precision and accuracy. The ICP-OES with gravimetric method has high precision and accuracy at low, medium, and high concentration levels. The testing precision of low, medium and high concentration levels are 0.44, 0.54, and 0.14%. The accuracy obtained for the three concentration levels was 98.03, 95.05, and 98.61%. Based on the ANOVA test, it was shown that the precision and accuracy at all concentration levels were not significantly different. This method can be recommended for routine testing of boron in geothermal fluids with low concentration and to avoid contamination of glassware made of borosilicate.

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