Comparison Between the Calibration and the Standard Addition Methods in Determining Dissolved Lead In Borobudur’s Control Tanks Water by Flame Atomic Absorption Spectrophotometry (F-AAS)

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Abstract

The use of the calibration and of the standard addition methods in determining dissolved lead in Borobudur’s control tanks water were compared. The aim of the study was to develop the standard addition method to determine very low concentrations of dissolved lead using Flame Absorption Spectrophotometry (F-AAS). Sampling was executed from five points: a point at the south side, a point at the south west, and three points at the north of the Borobudur Temple. The linearities of both curves were compared. The linearity of the calibration curve was found to be 0.957092, while of the standard addition had a linearity of ≥ 0.995 (except sample AS). Both methods gave different dissolved lead concentrations. The result of the calibration method was higher than that of the standard addition method.

Keywords: calibration; standard addition; dissolved lead

1. Introduction

Lead (Pb) is a heavy metal that is found 0.0002% in the world as galena (PbS)\textsuperscript{1}, cerrucite, or anglecite\textsuperscript{2}. It is versatile with melting point of 327°C. It also corrosion resistance so it can be used as geotextile material, as used in foundation construction of Borobudur Temple. Concrete foundation was installed when second restoration to increase the carrying capacity of the land as well as equipped with drains and impermeable layer. Lead sheet was placed under reliefs as high as hallway to prevent water capillary to the surface relief\textsuperscript{3}. The lead layer was to distribute the pressure among the rocks that had uneven contour\textsuperscript{4}.

The use of lead in the Borobudur’s drain construction may cause pollution. Lead is soluble in acidic water, especially in the presence of HNO\textsubscript{3}. Acidic rain water can seep and accumulate at lead layer. Direct contact between lead layer and the rain water for lasting time may caused lead layers dissolution forming Pb(NO\textsubscript{3})\textsubscript{2}. Dissolved lead can seep into drain and can seep to the surface relief. Continued contact between dissolved lead on the surface relief with carbonate, sulfate, and chloride ions create white deposits of PbCO\textsubscript{3}, PbSO\textsubscript{4} and PbCl\textsubscript{2}. The lead salt deposits can damage the rock and partly carried by flow water and enter into drain that ended at control tanks.

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Dissolved lead is determined using Flame Atomic Absorption Spectrophotometry (F-AAS) by standard addition method. This development is performed to determine a very low concentration of dissolved lead, considering F-AAS has a low sensitivity for lead parameter. The results of the determination of dissolved lead by standard addition are compared against the results of the calibration method as the primary method of determination of dissolved lead in Borobudur Conservation Agency.

2. Materials and Methods

2.1. Structure Materials

All samples are taken from five sampling points of Borobudur’s control tanks: a point at south side, a point at southwest, and three points at north of Borobudur Temple. Titrisol Pb 1000 mg and HNO₃ 70.5% 1.42 g/mL are purchased from Merck. The aquabidest are from PT Ikapharmindo Putramas.

2.2. Sample Preparations

Samples are filtered using 0.45 μm pore filter and acidified by HNO₃ until pH < 2. Acidification can preserve the samples until 6 month at 28°C.

2.3. Determination of Dissolved Pb by Calibration Method

Six different concentrations (0,0 – 0,8 mg/L) solutions of Pb are prepared. The absorption of standard solutions and samples are measured by F-AAS at 283.3 nm.

2.4. Determination of Dissolved Pb by Standard Addition Method

The multiple point standard addition use 10 mg/L standard Pb for spiking 10 mL original water sample respectively. All samples are diluted to 100 mL before measuring the signal.

3. Results and Discussion

Dissolved lead is a kind of some parameters that routinely determined in Borobudur’s control tanks water during rainy season to discover the lead dissolvation by acidic rain water. The qualities of five water samples are determined and presented in Table 1. The result shows that all parameters are in conformity with quality standards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard</th>
<th>Unit</th>
<th>Sample Code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>S</td>
</tr>
<tr>
<td>pH</td>
<td>6 – 9⁹)</td>
<td></td>
<td>7.08</td>
</tr>
<tr>
<td>T</td>
<td>≤ 38⁸)</td>
<td>°C</td>
<td>28</td>
</tr>
<tr>
<td>TDS</td>
<td>2000⁹)</td>
<td>ppm</td>
<td>93.86</td>
</tr>
<tr>
<td>Salinity</td>
<td></td>
<td>ppm</td>
<td>91.79</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1750 – 2250⁹)</td>
<td>μS/cm</td>
<td>100.8</td>
</tr>
</tbody>
</table>
3.1. Determination of Dissolved Pb by Calibration Method

The result of calibration standard measurement with various concentrations 0.0; 0.1; 0.2; 0.4; 0.6; and 0.8 mg/L of Pb is presented in Figure 1(a). The calibration curve equation is obtained as equation (1). This equation has coefficient correlation (R) of 0.957092 and coefficient determination ($R^2$) of 0.916025.

$$y = 0.007039x - 0.00043$$

Limit detection is determined by a linear regression line of the calibration curve by the equation (2) with residuals standard deviation $s_{y/x}$ and 3 factor value is according to IUPAC recommendation for 90% confident level. The limit detection (LoD) and limit of quantitation (LoQ) of standard calibration curve of Pb are 0.3130 mg/L and 1.0371 mg/L. The limit detection (LoD) shows the smallest concentration of analyte that can be detected in the sample with estimation of bias and imprecision at a very small concentration of the analyte. Meanwhile, the limit quantification is the lowest concentration of analyte that can be detected precisionly and accuratively. The LoQ is determined by equation (3).

$$\text{LoD} = \frac{3s_{y/x}}{\text{slope}}$$

$$\text{LoQ} = \frac{10s_{y/x}}{\text{slope}}$$

3.2. Determination of Dissolved Pb by Standard Addition Method

Standard addition solusions is made by adding a standard solution to the sample. Besides being able to overcome the samples matrix interference, this method also can be used to determine low concentration of analyte. As shown in Fig. 1(b), 0 mg/L standard addition solution gives respond uptake because it has contained the analyte of sample.

All correlation regression equation of standard addition method have met the minimum requirements of SNI 6989.8:2009 ($R \geq 0.995$), except for AS sample code. The regression equation is used to determine $x$-intercept, the value of $x$ at $y = 0$. Concentration of analyte is determined from the value of $x$-intercept multiplied by 10 times dilution factor.
3.3. Linearity Comparison of Calibration and Standard Addition

Harmita explain that the ability of analytical methods to provide a proportional response to the analyte concentration can be expressed by linearity. Linearity can be determined from the correlation coefficient of the curve. According to Figure 1(a), the coefficient correlation (R) of calibration method is 0.957092. It does not meet the minimum correlation value of SNI 6989:8: 2009 (R ≥ 0.995) (Indonesian National Standard, 2009), but it still acceptable statistically (R> 0.95). This is due to the low sensitivity of the calibration method (slope 0.007039) with a high LoD (0.3130 mg/L) so that the F-AAS is not accurately able to detect very low concentration of lead. On the other hand, the correlations of all standard addition curves are ≥0.995 has met these requirements, except for AS. The addition of sample analyte cause the concentration of lead standard solution increases so that the measured signals are also increased. This causes the sensitivity of the standard addition method is better than the sensitivity of the calibration method. This confirms the advantage of standard addition method to determine very low levels of analyte.

3.4. Comparison of Calibration and Standard Addition Results

As shown in Table 2, both methods give different results so it is not necessary a statistical test. Results of dissolved lead concentration corresponding to calibration method are greater than the results of standard addition method. However, both results still meet for Class II effluent standards according KEPMENLH No. 51/1995 (lead content <1 mg / L)(KLH, 1995).

Table 2. Dissolved Pb Concentration by Calibration and Standard Addition Methods

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Calibration (mg/L)</th>
<th>Standard Addition (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.1943</td>
<td>0.1628</td>
</tr>
<tr>
<td>BD</td>
<td>0.2492</td>
<td>0.0591</td>
</tr>
<tr>
<td>U1</td>
<td>0.3915</td>
<td>0.0335</td>
</tr>
<tr>
<td>U2</td>
<td>0.5336</td>
<td>0.0902</td>
</tr>
<tr>
<td>U3</td>
<td>0.6263</td>
<td>0.0460</td>
</tr>
</tbody>
</table>

LoD = 0.3130 mg/L

Conclusions

Both method give different dissolved lead concentrations. Results of calibration method is more higher than standard addition method. Meanwhile, the linearity of standard addition method are better than calibration method to determine a very low concentration of dissolved lead using F-AAS.

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References


