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Research Article

Comparison between Calibration and Addition Method of Lead and Chromium Total Testing in Textile Industrial Wastewater using AAS

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Abstract

Most of the wastewater from the textile industry in Indonesia has a negative impact on the environment and society. The wastewater contains heavy metals such as lead (Pb) and total chromium (Cr-Tot) from the coloring process. Pb and Cr-Tot parameters testing usually use Atomic Absorption Spectrophotometer (AAS). The purpose of this study was to compare between the calibration and the addition method to test the metal parameters of Pb and Cr-Tot contained in wastewater of textile industry of PT. X. Calibration method is often use for heavy metal concentration test than addition method. However calibration method is not frequently used for low concentration while addition method can be used for that. The difference between two methods is in the procedure. The concentrations of Pb and Cr-Tot using calibration method were 0.058 mg/L and 0.018 mg/L, respectively. Meanwhile, the concentrations of Pb and Cr-Tot using the addition method were 1.1419 mg/L and 1.1036 mg/L, respectively. Based on this research, the addition method gives a relatively better value and fulfills the interval requirements in the AAS readings for low Pb metal concentrations.

Keywords: AAS, addition method, calibration method, textile industry

1. Introduction

The textile industry in Indonesia is a rapidly growing industry to meet human needs. However, the textile industry has the potential to pollute the environment such as the waste produced in solid, liquid, or gas forms. Therefore, textile industry waste must be handled properly to minimize environmental pollution (Yoga and Nida, 2020). Textile industry waste comes from a series of dyeing processes and sludge from textile industry wastewater treatment plants (Rahmaulina et al, 2022).

According to Fita (2006) the coloring process is a process that has a strong polluting power due to the use of coloring materials. Dyes that are often used by the textile industry are remazol black, red, and golden yellow. The three dyes are quite stable so it is difficult to degrade in the waters. When the coloring process takes place, the dye is only used 5% while the rest is wasted as waste(Hasti, 2014). The waste is a synthetic chemical compound that is proven to be able to pollute the environment, one of which is heavy metal lead (Pb) and total chromium (Cr-Tot).

In the textile industry, Pb and Cr-Tot are used as a mixture of dyes, such as white color from Pb $(OH)_2.2PbCO_3$ and red color from Pb_3O_4 (Latifah et al., 2014). Pb metal is a neurotoxin that can enter and accumulate in the human or animal body, so the danger to the body is increasing (Kusnoputranto, 2006). In addition, high concentrations of Pb can cause the photosynthesis process to be disrupted and result in reduced production of a plant. Meanwhile, Cr-Tot metal is a metal that is unstable in oxygen, often used to give a shiny impression, and is used as a dye or paint. High concentrations of Cr-Tot can cause various health effects such as allergies, nasal irritation, and nosebleeds. Cr has low toxicity, but in metal form Cr-Tot is toxic (Harahap, 2011). Besides being used as a colorant, some literature shows that Pb and Cr-Tot metals are resistant to washing and sunlight (Kusnoputranto, 2006).

According to Ida et al (2014), the calibration method is a method that is often used in determining heavy metal concentrations. However, this method has weaknesses in detecting low concentrations of heavy metals and the occurrence of systematic errors such as measurement results that are not close to the actual value, so the use of the calibration method is less able to increase the sensitivity of the method. Therefore, other methods are needed that are expected to minimize these conditions. One other method for determining Pb and Cr-Tot metals is the standard addition method (Agung et al., 2012). According to Agung et al (2012), the standard addition method is a method by adding a standard solution to a number of samples to minimize errors caused by differences in environmental conditions (matrix) of samples and standards so that the measurement results are close to the actual value. The concentration of the standard solution is already known with certain quantity. The standard addition method has long been known, but is still rarely used. This addition method is suitable to be applied in determining environmental pollution which is very complex in nature (Syahputra, 2004). This study was conducted to compare the calibration method and the addition method in testing the parameters of Pb metal and Cr-Tot metal using AAS (Atomic Absorption Spectrophotometry). The results of the parameter testing were compared with ASTM E 663-86 1991 on Standard Practice For Flame Atomic Absorption Analysis.

2. Methodology

2.1 Sample Collection and Preparation

The sample used in this study is the WWTP inlet liquid waste in the textile industry of PT. X. Sampling was carried out in July 2021. The sample was poured into 10 jerry cans. Sample testing was carried out in the Bandung National Research and Innovation Agency (BRIN) laboratory by taking 1 L from each jerry can. Testing of Pb and Cr-Tot metal parameters using the calibration method was carried out without filtering, while the addition method was filtered with 0.45 μm porous filter paper. The filtering was done to remove solids and colloids (Ida et al., 2014).

2.2 Standard Solution Work Procedure

2.2.1 Pb Metal Standard Solution

The procedure for making Pb standard solutions for the calibration method refers to SNI 6989.8: 2009, namely making standard solutions of at least 3 different concentrations that are in the measurement range. The standard solution was made with concentrations of 0.2 ppm; 0.4 ppm; 0.6 ppm; and 1 ppm (Brian, 2020). How to make the standard solution series begins with making a standard solution. The standard solution is made by pipetting the standard solution of $Pb(NO3)2$ 1000 ppm as much as 5 mL into a 50 mL volumetric flask, then added distilled water to the exact limit mark and then homogenized. So that the 100 ppm standard solution is ready to use. After the 100 ppm standard solution is ready to use, a 10 ppm standard solution is made by pipetting 5 mL of 100 ppm standard solution into a 50 mL volumetric flask, then adding distilled water to the exact limit mark then homogenized. So that the 10 ppm standard solution is ready to use to make a series of Pb calibration standard solutions.

After the 10 ppm standard solution is ready to use, a standard solution series is made, namely 0.2 ppm; 0.4 ppm; 0.6 ppm; and 1 ppm by pipetting the 10 ppm standard solution as much as 0.5 mL; 1 mL; 1.5 mL; and 2.5 mL into each 25 mL volumetric flask. Then added distilled water until the limit mark and homogenized then ready to be measured for the standard curve. The four standard solutions were then put into each sample tube and the absorbance was measured using AAS-Light Shimadzu ASC-7000 at a wavelength of 283.3 nm.

The procedure for making the standard solution of the addition method refers to SNI 6989.8: 2009 as well as research conducted by Harjito (2019) and Ida, et al (2014). Similar to the preparation of Pb standard calibration solution, Pb standard addition solution is made from standard solution. The preparation of the standard solution adapts to the preparation of Pb standard solution in the calibration method, which is made by pipetting the Pb(NO3)2 1000 ppm standard solution as much as 5 mL into a 50 mL volumetric flask, then adding distilled water to the exact limit mark and then homogenizing, so that the 100 ppm standard solution is ready to use. After the 100 ppm standard solution is ready to use, a 10 ppm standard solution is made by pipetting 5 mL of 100 ppm standard solution into a 50 mL volumetric flask, then adding distilled water to the exact limit mark then homogenized. So that the 10 ppm standard solution is ready to use to make the Pb addition standard solution series.

After the 10 ppm standard solution is ready, a standard solution series is made, namely 0.8 ppm; 1.0 ppm; 2.0 ppm; 3.0 ppm; and 4.0 ppm which refers to the Pb test (Ida et al., 2014). The five standard solutions were made by pipetting 10 mg/L standard solution as much as 2 mL; 2.5 mL; 5 mL; 7.5 mL; and 10.0 mL into each 25 mL volumetric flask. Then added distilled water until the limit mark and homogenized, then ready to be measured for the standard addition curve. Each standard solution was measured for absorbance using AAS-Nyala Shimadzu ASC-7000 at a wavelength of 283.3 nm.

2.2.2 Cr-Tot Metal Standard Solution

The procedure for making Cr-Tot standard solution refers to SNI 6989.17: 2009, namely making a standard solution of at least 3 different concentrations that are in the measurement range. The standard solution series used are 0.1 ppm; 0.2 ppm; 0.4 ppm; 0.6 ppm; and 1.0 ppm which refers to the Cr-Tot test (Harjito, 2019). The solution series was made from a standard solution. Cr(NO3)2 standard solution 1000 ppm was pipetted as much as 5 mL into a 50 mL volumetric flask for 100 ppm standard solution, then added distilled water to the exact limit mark and then homogenized. After the 100 ppm standard solution is ready to use, then pipetted as much as 5 mL of 100 ppm standard solution into a 50 mL volumetric flask, then added distilled water until homogeneous. So that the 10 ppm standard solution is ready to use to make the Cr-T calibration standard solution series.

After the 10 ppm standard solution is ready, a standard solution series of 0.1 ppm; 0.2 ppm; 0.4 ppm; 0.6 ppm; and 1.0 ppm is made by pipetting the 10 ppm standard solution as much as 0.25 mL; 0.5 mL; 1 mL; 1.5 mL; and 2.5 mL into each 25 mL volumetric flask. Then added distilled water until it is completely dissolved and ready to be measured for the standard curve. The five standard solutions were then put into each sample tube and the absorbance was measured using AAS-Light Shimadzu ASC-7000 at a wavelength of 357.9 nmWhile the procedure for making standard solutions of the addition method refers to SNI 6989.8: 2009 and previous studies such as research conducted by Harjito (2019) and Ida et al (2014). Similar to the Pb addition standard solution series made from 10 ppm standard solution. Cr-Tot addition standard solution series were made with concentrations of 0.8 ppm; 1.0 ppm; 1.2 ppm; 3.0 ppm; and 4.0 ppm. The method of making the solution series is pipetted 10 ppm standard solution as much as 2 mL; 2.5 mL; 3 mL; 3.5 mL; and 4 mL into each 25 mL volumetric flask. Then added distilled water until homogeneous and ready to be measured. The five standard solutions were put into each sample tube. Then the absorbance was measured using AAS-Light Shimadzu ASC-7000 at a wavelength of 357.9 nm.

2.3 Working Procedure Consentration Pb dan Cr-Totin Liquid Waste Samples

2.3.1 Determination by Calibration Method

The determination at this stage is the same as the working procedure for the standard solution of Pb and Cr-Tot metal calibration method, which refers to SNI 6989.8: 2009 and SNI 6989.17: 2009.

Samples of textile industry liquid waste were pipetted as much as ± 10 mL into the sample tube. Then the absorption was measured using AAS-Nyala Shimadzu ASC-7000 at a wavelength of 283.3 nm for Pb metal and at a wavelength of 357.9 nm for Cr-Tot metal. The measurement was done once (simplo).

2.3.2 Determination by Addition Method

The determination at this stage refers to previous studies such as Harjito (2019) and Ida, et al (2014). Samples were made by pipetting 1 mL of liquid waste into a 25 mL volumetric flask (a) and doing the same for another 25 mL volumetric flask (b). Then added 2 ppm standard solution for Pb metal (a) while Cr-Tot metal added 24 mL of 1 ppm standard solution (b) until the exact limit mark then homogenized. The selection is based on the minimum AAS reading requirements, which are 1 mg/L for Pb metal while 0.2 mg/L for Cr-Tot metal. After homogenized, put into the sample tube, then measured the absorption using AAS-Light Shimadzu ASC-7000 at a wavelength of 283.3 nm for Pb metal and at a wavelength of 357.9 nm for Cr-Tot metal.

2.4 Calculations

The calculation for the calibration method can be seen in equation 1 which refers to SNI 6989: 2009. The equation consists of the concentration of Pb or Cr-Tot metal in wastewater (C) and the dilution factor if dilution is carried out on the test (f).

$$\text{Concentration Pb (mg/L)} = C \times f \quad (1)$$

While the calculation for the addition method can be seen in equation 2. The equation consists of the sample concentration (Cx) and the standard concentration used (Cs) in units of (mg/L), the absorbance of the sample (Ax) and the absorbance of the standard used (As+x), as well as the volume of the sample (Vx) and the volume of the standard used (Vs) (Garicia and Baez, 2012).

$$Cx = \frac{Ax * Cs * Vs}{(As+x-Ax) * Vx} \quad (2)$$

2.5 Data Analysis

According to Chan et.al., (2004) linearity is the ability of an analytical method to obtain test results that match the concentration of the analyte in the sample in a certain concentration range. This can be done by making a curve from a series of standard solutions that have known concentrations. The line equation used on the curve is y = a + bx. The equation will produce a coefficient of determination (R^2). The minimum linearity determination uses 1 or more different concentrations with a value that meets the requirements, namely $R^2 > 0.9970$ or close to 1 (Harjito, 2019). The value of R^2 is declared good and has a good linearity value if the value is close to 1. The interpretation of the R^2 value can be seen in **Table 1**. The standard solution curve must be linear because if the curve is no longer linear, the error in the results of the comparative test analysis will be greater (Harahap, 2011).

The limit of detection (LoD) is the smallest amount of analyte in a sample that can be detected and gives a significant response compared to the blank. The limit of detection indicates the quantitation concentration that must be detected with precision and accuracy (ICH, 2005). Sensitivity is an analytical method that can be expressed within the LoD limit (Iwan et al., 2011).

Table 1. Interpretation Coefficient Determination (R^2)

Coefficient Interval	Relationship Level
0.00 – 0.199	Very Low
0.20 – 0.399	Low
0.40 – 0.599	Medium
0.60 – 0.799	Strong
0.80 – 1.000	Very Strong

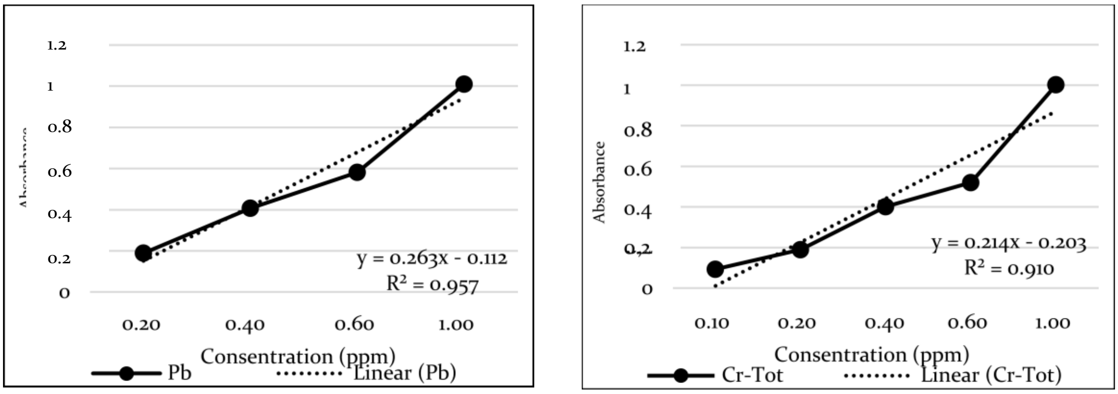
Source: Sugiyono, 2018

3. Results and Discussion

The absorbance results of the Pb and Cr-Tot calibration standard solutions can be seen in **Table 2**. The absorbance is plotted against the standard solution concentration series in the form of a Pb and Cr-Tot standard calibration curve which can be seen in **Figure 1**.

Table 2. Absorbance of Pb and Cr-Tot standard solution by calibration method

No	**Metal Pb**		**Metal Cr-Tot**	
	Concentration (x) (ppm)	**Absorbance (y)**	**Concentration (x) (ppm)**	**Absorbance (y)**
1.	0.2	0.1889	0.1	0.0932
2.	0.4	0.4068	0.2	0.895
3.	0.6	0.5811	0.4	0.4015
4.	1.0	1.0097	0.6	0.5204
5.	-	-	1.0	1.0022



(a) **(b)**

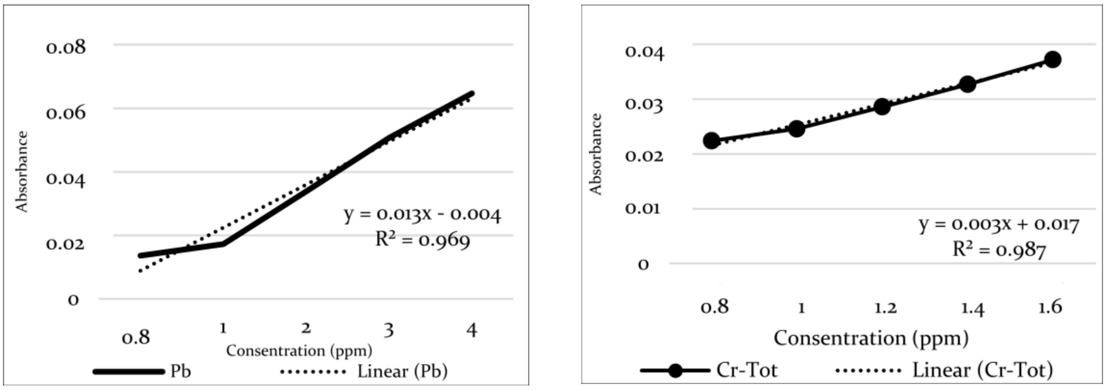
Figure 1. Pb standard calibration curve (a) and Cr-Tot standard calibration curve (b)

In **Figure 1 (a)**, it can be seen that the Pb standard calibration curve gives the line equation y = 0.2637x - 0.1126. Linear regression analysis shows a coefficient of determination (R^2) of 0.9572. While in **Figure 1 (b)** shows that the Cr-Tot standard calibration curve gives a line equation y = 0.2249x - 0.2033 and an R^2 value of 0.9108. The R^2 value shows that the closeness of the linear regression line to the Pb standard solution series data is 95.72% while the closeness of the linear regression line to the Cr-Tot standard solution series is 91.08%. Both R^2 values are below the criteria for a linear curve. When compared to the statement of Harjito (2019) which states that the use of the method can be said to be linear in a certain concentration range (R^2 value > 0.9970). So it can be concluded that the Pb and Cr-Tot standard calibration curves are not linear which can cause the calibration method to be unable to accurately detect low levels of Pb and Cr-Tot metals (Harjito, 2009). However, the two R^2 values have a very strong level of influence between the concentration of Pb and Cr-Tot and the absorbance obtained (Sugiyono, 2012).

On the other hand, the absorbance results of the Pb and Cr-Tot addition standard solutions can be seen in Table 3. The absorbance is plotted against a series of standard solution concentrations in the form of Pb and Cr-Tot standard addition curves which can be seen in **Figure 2**.

Tabel 3. Absorbance of Pb and Cr-Tot standard solution by addition method

No	Pb Metal		Cr-Tot Metal	
	Concentration (x) (ppm)	**Absorbance (y)**	**Concentration (x) (ppm)**	**Absorbance (y)**
1.	0.8	0.0137	0.8	0.0224
2.	1.0	0.0173	1.0	0.0246
3.	2.0	0.0338	1.2	0.0286
4.	3.0	0.0507	1.4	0.0327
5	4.0	0.0647	1.6	0.0372



(a) **(b)**

Figure 2. Pb standard addition curve (a) and Cr-Tot standard addition curve (b)

In **Figure 2(a)**, it can be seen that the Pb standard addition curve gives the line equation $y = 0.0135x - 0.0046$ while the Cr-Tot standard addition curve gives the line equation $y = 0.0038x - 0.0178$ which can be seen in **Figure 2(b)**. Linear regression analysis showed R^2 values of 0.9692 for the Pb standard addition curve and 0.9873 for the Cr-Tot standard addition curve. The R^2 value indicates that the closeness of the linear regression line to the Pb standard solution series is 96.92% while the closeness of the linear regression line to the Cr-Tot standard solution series is 98.73%. The R^2 value is below the criteria for a linear curve, but the R^2 value obtained has a very strong level of influence between the concentration of Pb and Cr-Tot with each absorbance (Sugiyono, 2012). The value of R^2 on the Pb and Cr-Tot standard addition curve is closer to 1 than the Pb and Cr-Tot standard calibration curve. This is likely due to the addition of standard solution in the effluent sample can cause the concentration of the measured solution to increase so that the measured signal also increases. From this comparison, it can be concluded that the addition method has a good R^2 value and linearity compared to the calibration method. It is possible that the addition method can be used to determine low analyte concentrations.

After obtaining these equations, both the equations in the calibration method and the addition method were used to obtain the concentrations of Pb and Cr-Tot in the PT X textile industry wastewater which can be seen in **Table 4.**

Table 4. Comparison of Pb and Cr-Tot metals with AAS reading requirements

Heavy Metals	Limit Detection[a]	Sensitivity[a]	Optimum Concentration[a]	Calibration (mg/L)	Addition (mg/L)
Pb	0.05	0.5	1-20	0.058	1.1419
Cr-Tot	0.02	0.1	0.2-10	0.018	1.1036

Source: (a) ASTM E 663-86 tahun 1991 tentang Standard Practice For Flame Atomic Absorption Analysis

The concentrations of Pb and Cr-Tot using the calibration method were obtained at 0.058 mg/L and 0.018 mg/L. While the concentration of Pb and Cr-Tot using the addition method was obtained at 1.1419 mg/L and 1.1036 mg/L. Based on these data, the concentration of Pb and Cr-Tot using the calibration method is smaller than the addition determination method. **Table 4** shows that the test results of Pb and Cr-Tot metals using the calibration determination method do not meet the optimum concentration range. In contrast to the test results of Pb and Cr-Tot metals using the addition determination method that meets the requirements of the minimum detection limit, minimum sensitivity, and optimum concentration range. Seen from this side, testing using the addition method is considered legible in the AAS tool used while testing using the calibration method is considered illegible in the AAS tool because the data obtained is below the optimum AAS reading concentration range (Harjito, 2019).

Table 5. Pb and Cr-Tot metal testing results

Heavy Metals	**Calibration (mg/L)**	**Addition (mg/L)**	
		(Standard+Sample) (Cs+Cx)	**(Sample) (Cs)**
Pb	0.058	1.1419	0.0444
Cr-T	0.018	1.1036	0.1531

Based on **Table 5**, it can be seen that the data obtained using the addition method is calculated by subtracting the concentration of the standard solution added to the sample (spike) (Cs+x) and the concentration of the standard solution used (Cx). The concentration of the spike solution used in this method is 2 ppm for Pb and 1 ppm for Cr-T. However, these concentrations became different after being measured in the AAS, namely 1.0975 mg/L (Cs+x Pb) and 0.9505 mg/L (Cs+x Cr-T). Thus, the Pb and Cr-Tot concentrations in the effluent were 0.0444 mg/L and 0.1531 mg/L, respectively.

4. Conclusion

The test results of Pb and Cr-Tot metal parameters using AAS in the calibration method in the PT. X textile industry wastewater obtained concentrations of 0.058 mg/L and 0.018 mg/L. While the addition method obtained Pb and Cr-Tot concentrations of 1.1419 mg/L and 1.1036 mg/L. Based on the results obtained, the concentration of Pb and Cr-Tot using the addition method is greater than the calibration method. When compared to the AAS reading requirements, the addition method meets these requirements while the calibration method is below the standard requirements. So that low Pb and Cr-Tot metal parameter testing can be detected by the addition method. According to Anisa et al (2019) industry textile waste contains concentrations of heavy metals besides Pb and Cr-Tot metals. Based on that, it should test other metal parameters using calibration and addition methods and the test is carried out 2 times (duplo) with the aim of being a comparison and getting the final result (Afrissa, 2019).

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