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The Analysis of Manganese (Mn) in Waste Water Treatment (IPAL) of Coal Mine of PT Bukit Asam Indonesia

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Abstract

Wastewater from the coal mining process containing heavy metal manganese is bad for water body and health of living things around it. The South Sumatra Governor Regulation states that the content of iron (Fe) and manganese (Mn) must contain a maximum total of 7 mg/L and 4 mg/L before being released into the environment. This study aimed to verify the total dissolved Mn analysis method. Thirty-four (34) samples from the wastewater treatment plant pond were digested and measured by the Atomic Absorption Spectrophotometer (AAS) at a wavelength of 279.5 nm. The analysis performed were the precision, sensitivity, linearity, LOD detection limits and LOQ quantization limits. The measurement results showed the parameter value for a precision of 1.562%; linearity (coefficient of determination) standard curve 0.9939; sensitivity 0.0375; LOD 0.4287 g/mL; and LOQ 1.4291 µg/mL. In conclusion, the measurement data for the total dissolved manganese met the quality standards for wastewater stated in the Regulation of the Governor of South Sumatra No.8 of 2012 by applying the predetermined method.

Keywords: Manganese, LOD, LOQ, AAS, and Wastewater.

Abstrak (Indonesian)

Air limbah dari proses penambangan batubara yang mengandung logam berat mangan berdampak buruk bagi badan air dan kesehatan makhluk hidup disekitarnya. Peraturan Gubernur Sumatera Selatan menuliskan bahwa kandungan besi dan mangan. dengan total maksimum 7 dan 4 mg/L sebelum dialirkan ke lingkungan. Penelitian ini bertujuan untuk memverifikasi metode analisa total Mn terlarut. 34 sampel dari kolam instalasi pengolahan air limbah didestruksi dan diukur dengan Spektrofotometer Serapan Atom (SSA) pada panjang gelombang 279,5 nm. Analisa yang dilakukan yakni uji presisi, sensitivitas, linearitas, batas deteksi LOD dan batas kuantisasi LOQ. Hasil pengukuran menunjukkan nilai parameter untuk presisi 1,562%; linearitas (koefisien determinasi) kurva standar 0,9939; sensitivitas 0,0375; LOD 0,4287 µg/mL; dan LOQ 1,4291 µg/mL. Dapat disimpulkan bahwa data pengukuran total mangan terlarut telah memenuhi baku mutu air limbah dalam Peraturan Gubernur Sumatera Selatan No.8 tahun 2012 dengan menerapkan metode yang sudah ditetapkan.

Kata Kunci: Mangan, LOD, LOQ, dan Air Limbah.

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INTRODUCTION

Coal is one of the largest sources of energy globally. The content of coal is classified as organic mineral [1] and inorganic elements [2]. Mn [3], Fe [4], sulphate [5], dan Zn are inorganic compounds that are mostly contained in coal [6]. In addition, the inorganic metals are also abundant in coal seepage water in the form of dissolved ions [7] classified as waste.

Pollution in the form of coal waste water is processed in a Wastewater Treatment Plant (IPAL). Physically, the water to be discharged into the river looks clear and clean, however, the dissolved metal content in the wastewater needs to be analyzed to

determine its levels [8]. The mine water contains heavy metals such as manganese (II) (Mn^{2+}) which is abundant [9]. If water contaminated with manganese is consumed by humans it can be detrimental to health There are various ways to measure levels of manganese such as electrolysis, electrochemistry, and other methods [10]. However, the method used must be relevant to the capabilities of a laboratory and the standards set by the government. The testing of the Mn content in this study applied the modified SNI standard method through verification and validation of the Atomic Absorption Spectrophotometer (AAS), thus differentiating it from the other tests.

Wastewater Treatment Plants carried out by PT. Bukit Asam consists of three treatment ponds through a gradual draining process, after passing through the third pond, the waste water will be discharged into the river. Physically, the water to be discharged into the river looks clear and clean, however, the dissolved metal content in the waste water needs to be analyzed to determine the levels [11]. This test is needed to meet the water quality standard requirements that have been set by the government and as a form of concern for the parties concerned about the environment [12]. Testing the parameters of the Mn content in the waste water collected in the IPAL was very important, especially to reduce the manganese content in the wastewater before it was discharged to the mining area. This test was needed to meet the quality standards set by the government and as a form of concern for those who cared about the environment around mining. This study used the Atomic Absorption Spectrophotometer (AAS) in analyzing manganese metal absorption aiming to obtain linearity data from the analysis of results.

MATERIALS AND METHODS

Materials

Measurement of manganese content was carried out based on SNI: 6989.5: 2009. The tools used in this practical work were: Atomic Absorption Spectrophotometer, Mn Hollow Cathode lamp, 250 mL beaker glass, volumetric flasks of 100 mL, 200 mL, and 250 mL, Whatman No. 40 filter paper, with a pore size of 8 µm, measuring pipettes of 5 mL; 10 mL; 20 mL; 30 mL; 40 mL, and an electric heater, a glass funnel, and a spray flask.

Materials used in this practical work: Nitric Acid (HNO_3), Manganese standard solution (Mn 1000 mg/L), Argon gas, and distilled water.

Methods

Sampling

The sample to be analyzed was taken by the environmental management unit, derived from several different points of the inlet and outlet ponds, totaling 82 samples. They were then taken to the water/soil/dust/rock laboratory for the analysis with different parameters.

Sample Preparation

The sample was put into a 50-100 mL beaker and 5 mL of nitric acid was added. The solution mixture was then heated with an electric heating until almost dry (until the final volume ranged from 10-20 mL.) After heating, 50 mL of distilled water was added, put into a 100 mL volumetric flask through filter paper exactly at 100 mL with distilled water. The sample was then stored in a glass bottle and tightly closed.

Preparation of Manganese Standard Solution (Mn)

Manganese Standard Solution of 100 ppm, Mn 100 mg / L taken using a pipette, the 10 mL of standard 1000 ppm solution was put into a 100 mL volumetric flask which was then added 0.1 M nitric acid solvent until reaching the mark and getting homogeneous. Manganese Standard Solution 10 ppm, Mn 10 mg/L determined by the standard solution of manganese was pipetted with 50 mL, Mn 100 mg/L into a 500 mL volumetric flask. It was put exactly with the diluent solution to the mark. Standard Working Solution was 1; 2; 3; 4; 5 ppm measure with 100 ppm standard solution was prepared each with 1 mL burette; 2 mL; 3 mL; 4 mL; 5 mL, then put each of them into a 100 mL volumetric flask and added 0.1 M nitric acid solvent to the mark and had them homogenized.

Preparation of Calibration Curves

The AAS instrument was adjusted and then the gas was ignited as required in the test. The test method and cathode lamp were adjusted according to the test parameters (Mn = 279.5 nm). The internal calibration was carried out using the existing work standard solution to obtain maximum linearity (minimum correlation coefficient r = 0.99), if the r value was less than 0.99, the correction was made to the standard solution preparation and the conditions of the AAS instrument. If the appropriate linearity met the standard, the testing of the spike sample against the test parameters was continued, by reading the absorbance of the sample solvent (blank) and the sample solution.

Data Analysis

Precision Test

The already made absorbance of the standard solution was measured at an absorption wavelength of 279.5 nm for 5 repetitions. The accuracy was measured by calculating the standard deviation and the percentage of its relative standard deviation (coefficient of variation).

$$Sd = \sqrt{\frac{\Sigma(x - \bar{x})2}{n-1}} \quad (1)$$

Whereas :
SD : Deviation Standard
X_i : Absorbance
X : average absorbance
n : number of repetitions

$$RSD = \frac{SD}{x} \times 100\% \quad (2)$$

Whereas:
RSD : Relative Standard Deviation
SD : Deviation Standard
X : Absorbance

Linearity Test

The absorption of each standard solution was measured using an atomic absorption spectrophotometer at an absorption wavelength of 279.5 nm. Then the line equation was made using the linear regression method (y = ax + b). The variable a represented the slope of the lines of the five standard solutions (slope) and b represented the intercept. The linearity of the calibration curve was showed from the correlation coefficient (r).

Sensitivity Test

The sensitivity of the Atomic Absorption Spectrophotometer test tool was to measure the standard solution of Mn 3 ppm for 5 times. The result of the mean measurement was used to calculate the sensitivity with the equation.

$$S = 0{,}0044 \left(\frac{C}{A}\right) \quad (3)$$

Whereas:
S : Sensitivity Value
C : Solution Concentration
A : Solution Absorbance

Detection Limit Test (LOD)

The limit of detection (LOD) was statistically calculated from the linear equation y = ax + b of the standard curve or through the equation:

$$LOD = \frac{3\ SD}{a} \quad (4)$$

Whereas:
LOD : Detection Limit
SD : Deviation Standard

Quantization Limit Test (LOQ)

The limit of quantization (LOQ) was statistically calculated from the line equation y = ax + b from the standard curve or through equations:

$$LOD = \frac{10\ SD}{a} \quad (5)$$

Whereas:
LOD : Detection Limit
SD : Deviation Standard

RESULTS AND DISCUSSION

Precision Test

Precision is a measure of the dispersion (dispersion of a set of results), the proximity of a series of repeated measurements to each other. The precision is applied to iterative measurements so that the individual measurement results are distributed around the average value regardless of where the average is against the true value. This test was conducted by measuring the standard solution of manganese (Mn) at 3 ppm 5 times. The results of the precision test are presented in the following Table 1.

Table 1. Results of precision of manganese standard solution (Mn)

Concentration (ppm)	Absorbance
3	0.350
3	0.346
3	0.352
3	0.353
3	0.361
Average	0.352
SD	0.0055
RSD	1.562%

The results of the measurement show that the relative standard deviation value was 1.562%. The value obtained turned out to be quite good because it was smaller than the determined 2%. Therefore, the analysis of total dissolved metal manganese (Mn) in wastewater using HNO_3 digestion measured by atomic absorption spectrophotometer was very good.

Linearity Test

Linearity is a correlation coefficient between the concentration of the standard solution and the resulting absorbance which is a straight line. The analytical method that describes the ability of a tool to obtain the test results proportional to the analytical content of the tool in the test sample over a certain concentration range. The linearity test is conducted by making a calibration curve that can produce a regression line equation and the coefficient of determination to determine the relationship between the concentration of the standard solution and the resulting absorbance value.

Table 2. Absorbance of manganese standard solution (Mn)

Concentration (ppm)	Absorbance
1	0.146
2	0.259
3	0.361
4	0.520
5	0.611

Based on the results of the calibration test of the digestion method and atomic absorption spectrophotometer, the regression line equation of Mn was Y = 0.1111x + 0.0221 and the coefficient of determination of R^2 was 0.9939, meaning the value was close to 1, in other words, the use of this method could be used for dissolved metal analysis total manganese (Mn) with good results.

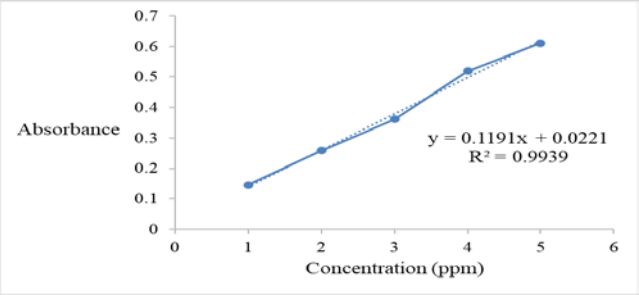

Figure 1. Calibration curve of manganese standard solution (Mn)

Sensitivity Test

The sensitivity of the Atomic Absorption Spectrophotometer test instrument was obtained by measuring the standard solution of Mn 3 ppm for 5 times. The mean measurement result was used to calculate the sensitivity with the formula S = 0.0044 (C/A), where C was the standard concentration of manganese metal (Mn) 3 ppm; A is the average value of 3 ppm standard metal manganese (Mn) absorption.

Based on the calculation of the sensitivity test, the manganese metal (Mn) sensitivity test value was 0.0375 smaller than the factory sensitivity value of 0.75, in other words, the atomic absorption spectrophotometer test equipment was still suitable for use as a test tool with the sensitivity gain still below the required limit.

Detection Limit Test (LOD)

The element detection limit is defined as the lowest detectable concentration of analyte. The element detection limit is determined based on the statistical calculation of the calibration curve of each element obtained. The standard element calibration curve obtained the linear line equation y = ax + b. The linear line equation obtained the amount of absorption, the value of the standard deviation, the amount of absorption at the detection limit, and the level at the detection limit.

Table 3. The results of calculating the absorbance data of the standard metal manganese (Mn) without the accuracy and precision.

Concentration (ppm)	Absorbance			
(x)	(y_i)	y	y_i-y	$(y_i-y)^2$
1	0.146	0.1412	0.0048	0.000023
2	0.259	0.2603	-0.0013	0.000002
3	0.361	0.379	-0.0184	0.000339
4	0.52	0.4985	0.0215	0.000462
5	0.611	0.6176	-0.0066	0.000044
	Total			0.0009

Based on the calculation results, the detection limit value was 0.4287 ppm. This shows that the atomic absorption spectrophotometer can still read the absorption of the analyte at a concentration of 0.4287 ppm but not accurately and precisely.

Quantization Limit Test (LOQ)

The limit of quantization is defined as the lowest concentration of analyte in a sample that can still meet the criteria for precision and accuracy. The result of the quantization value calculation showed that the value was 1.4291 ppm. In conclusion, the smallest concentration of analyte in the sample that can still meet the criteria for precision and accuracy is 1.4291 ppm.

Discussion

Testing at the Laboratory of PT. Bukit Asam was conducted to determine several parameters for testing wastewater including pH, total dissolved solids, ferrous metals and manganese. The following

discussion is an analysis of manganese content of wastewater which is useful for controlling manganese metal content before waste water is discharged to final disposal. The samples analyzed consisted of 81 samples consisting of 34 inlets and 47 outlets. The inlet sample was from the mine waste water storage pond before the processing. Meanwhile, the outlet sample was from the collection point for the wastewater that was already processed previously.

The acid mine wastewater treatment at PT. Bukit Asam was carried out through three processing ponds. First, the acid mine drainage entered the siltation pond. Second, the neutralization pond used quicklime and sodium hydroxide. The amount of lime that had to be added to neutralize acid mine drainage was found out by using the Jartes method. Tolonen et al [13] found that quicklime can decrease Mn concentration up to 99% in mining wastewater. Third, the holding pond for the phytoremediation process utilized the plants resistant to acidic conditions useful for absorbing heavy metals. Whereas, it has high potential in remediation process of contaminated area using hyper accumulator plants to absorb the heavy metals [14]. *Eichhornia crassipes* was the chosen plant for phytoremediation because it was effective and low cost. Furthermore, *E. crassipes* leaves effectively become the bio-indicator in accumulating the Mn and other metals from the holding pond [15]. After going through the processing pond, the result was accommodated in the outlet storage pond to analyze the above four parameters.

The samples to be analyzed in the laboratory were prepared in advance. The number of heavy metals were reduced with the addition of nitric acid and heated. The addition of nitric acid was intended to dissolve the metal analyte [16] and removed the disturbing substances in the water sample with the aid of an electric heater. The heating aimed to find out the total manganese metal [17], both dissolved and undissolved metals so that they were completely reduced. Then, the water sample was filtered and diluted in a hundred milliliter dilution flask added with distilled water. The filtering functioned to filter out impurities [18] and large particles to make it easier during the use of the spectrometer. The sample that was already prepared was then measured for its absorbance using the atomic absorption spectrometer.

The standard solution of 100 ppm manganese was made by diluting the manganese solution with distilled water, then making the manganese working solution according to the procedure. The blank solution used was a pH 2 solution made from distilled water added with nitric acid until the pH reached two. The testing with an atomic absorption spectrometer began by adjusting the cathode lamp and its wavelength according to the test parameters. The manganese cathode lamp had a wavelength of 279.5 nm. Then it was calibrated with a blank and manganese standard solution to find out a standard solution with the maximum linearity value. After the determination of the standard solution, the sample was analyzed on the atomic absorption spectrometer and the absorbance value was recorded.

The obtained results were the value of manganese metal in the sample inlet was very high because it did not enter the processing process. While the results for the sample outlets were in accordance with the Governor's Decree No. 18 regarding coal mining where the maximum Mn content is 4 ppm. An appropriate number of Mn concentration was discovered because of the treatment in the processing pond. The results were as follows, then they are used as a reference for treating acid mine drainage before they are discharged to the environment.

CONCLUSION

From the results of the calculations carried out, the validation parameter values for the manganese metal (Mn) analysis method using the atomic absorption spectrophotometer method were obtained, namely precision, sensitivity, linearity, LOD detection limit and LOQ quantization limit. From these results it can be concluded that the analysis method of total dissolved metal element manganese (Mn) by destruction with nitric acid using an atomic absorption spectrophotometer is declared valid.

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