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TEST METHOD VERIFICATION OF Fe AND SiO₂ IN INDUSTRIAL WATER BY UV-VIS SPECTROPHOTOMETRY AT PT KRAKATAU STEEL

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Abstract

It has been conducted the test methods verification of Fe and SiO₂ in industrial water using UV-Vis spectrophotometer at PT Krakatau Steel. Verification parameters tested were linearity, precision, accuracy, and detection limit. The results show the value of linearity, precision, accuracy and detection limits for testing Fe are respectively 0.996; 3.803%; 87.94% and 0.048 mg/L while for SiO₂ consecutive tests was 0.998; 2.014%; 100.755% and 0.010 mg/L. The results of test methods verification of Fe and SiO₂ meet the requirements and can be accepted as a method for routine testing in the chemical laboratory of PT Krakatau Steel.

Key words: verification, industrial water, Fe, SiO₂, UV-Vis spectrophotometer

INTRODUCTION

Water is one of the utilities that support industrial process. In the industry, especially the chemical industry, water has several functions: water as the industrial household, process water, cleansing water and water steam generator (boiler feed water) (Widyatmiko, 2005). According to Mussey (1961), process water is water that comes into contact with an end product or with materials incorporated into an end product; cooling water is water used exclusively for cooling; boiler-feed water is water introduced into boilers for conversion to steam; and sanitary and service water is water used for drinking, showers, general cleaning, and flushing wastes.

PT Krakatau Steel is the first and largest integrated steel industry in Indonesia, located in Cilegon, Banten. The products of PT Krakatau steel are hot rolled coils, cold rolled coils an wire rod steel wich are the raw material for the next industries. Large quantities of water are required to produce steel, typically 180-200 m³ of water per ton of steel produced.

Water is used in the steel industry for direct contact cooling and cleaning of the steel in process, for cooling the process off gases, for product rinsing, and for process solution makeup; however, the vast majority of the water used in steel making is for non-contact cooling of associated processing equipment. Water is also used for steam and power generation, potable uses, and dust and moisture control (Lehrman et.al, 1999).

Because water has an important role in the steel industry, it will need special requirements such silica and Fe content. High concentration of silica in boiler feed water is harmful as silica tends to deposited as glassy and hard scale in boiler and cooling water systems. While high concentrations of Fe can causes the boiler and water line deposits as iron oxide (Fe_2O_3 or Fe_3O_4). Iron and steel industries in the United States use a water supply with a maximum SiO_2 and Fe content for cooling and processing water in steel plants are 30 and 6.3 ppm; for cooling and processing in hot-rolling mills are 21 and 0.4 ppm, and for boiler feed in steel plants are 30 and 6.3 ppm (Walling and Ottis, 1967). Meanwhile, according to the American Society of

Mechanical Engineers (ASME) boiler feed water quality requirements are a maximum of 0.1 ppm for Fe, while the requirements for boiler water is a maximum of 150 ppm for silica.

Therefore, it is necessary to determine the water used to supply in an effort to control the quality of water that can be prevented greater losses. To analyze the content of SiO_2 and Fe can be done by using UV-Vis Spectrophotometry method. The standard method used in chemical laboratory of PT Krakatau Steel for determination of iron content is in accordance with ASTM D.1068.84 while for SiO_2 content is in accordance with SOP.3133 QP02 019.

Because these methods are routinely used, it should be conducted the methods verification to verify the performance of both standard methods. In addition, methods verification are needed to prove that the laboratory is able to demonstrate the analysis methods to produce valid data. This paper aims to verify the test method of Fe and SiO_2 in the industrial water of PT Krakatau Steel with the parameters linearity, precision, accuracy and detection limit.

RESEARCH METHOD

Materials

All chemicals are analytical grade and used without further purification. Hydrochloric acid (HCl), hydroxylamine hydrochloride ($NH_2OH.HCl$), ammonium acetate (CH_3COONH_4), 1,10-phenanthroline ($C_{12}H_8N_2$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$), oxalic acid ($H_2C_2O_4$), and ascorbic acid ($C_6H_8O_6$).

Test Method Verifikasi of Fe

Linierity test is done by determining the correlation and determination coefficient for calibration curve of Fe standard solution. Series of standard solutions prepared from stock solutions of iron 10 mg/L by adding 0; 1; 2; 3; and 4 mL in a 100 mL volumetric flask. Then added with 2 mL HCl : water (1:1 v / v), 1 mL hydroxylamine hydrochloride 10%, 10 mL ammonium acetate 10%, 10 mL fenantrolin 0.1% and filled with distilled water to the mark. The solution was allowed to stand 10 minutes and the absorbance was measured by UV-Vis spectrophotometry at 510 nm.

Precision test was done by measuring the iron content in the sample seven times. A total of 50 mL of industrial water sample put into a 100 mL volumetric flask and then added 2 mL HCl: water (1:1 v/v), 1 mL hydroxylamine hydrochloride 10%, then heated to boiling. The solution was cooled and added 10 mL ammonium acetate 10%, 10 mL fenantrolin 0.1% then filled with water to the mark. The solution was homogenized and the absorbance was measured at 510 nm. % RSD values calculated to determine the value of precision.

Accuracy test was done by determining the value of %recovery. Procedure used was the same with precision test procedures but 10 mL of stock solution of iron 10 mg/L was added as a spike. Detection limit was done by measuring the absorbance of the reagent blank seven times. The procedure was performed the same as the test procedure of precision but was not use industrial water samples.

Test Method Verifikasi SiO₂

Linierity test was done by determining the correlation and determination coefficient for calibration curve of SiO_2 standard solution. Series of standard solutions prepared from the silicate stock solution 10 mg/L by adding 0; 5; 10; 20; 30 and 40 mL in 250 mL volumetric flask. Then added with 5 mL ammonium molybdate 5% and aged 4 minutes. Then added 5 mL oxalic acid 5% and allowed to stand 2 minutes. Furthermore, added with 5 mL ascorbic acid 4% and distilled water to the mark. Solution was homogenized and the absorbance was measured by UV-Vis spectrophotometry at 815 nm.

Precision test was carried out by the same procedure to the linearity test by replacing the standard solution to 10 mL industrial water sample. Absorbance measurements performed seven times. Accuracy test procedure used was the same as precision test procedures but 10 mL of the standard solution silicate 10 mg/L added as a spike. Absorbance measurements were also carried out seven times. The absorbance of the reagent blank were measured seven times by the same procedure with precision test but without samples water for determining the detection limit.

RESULT AND DISCUSSION

The principle of the determination of Fe with ASTM D.1068.84 method is the reduction of Fe^{3+} in the sample to Fe^{2+} by hydroxylamine hydrochloride in acidic conditions. Fe^{2+} ions then reacted with 1,10-fenantrolin form reddish orange complex compounds and absorbance was measured at 510 nm. This complex compound is very stable at pH 4-6 which is maintained by the addition of ammonium acetate. The reaction is as follows:
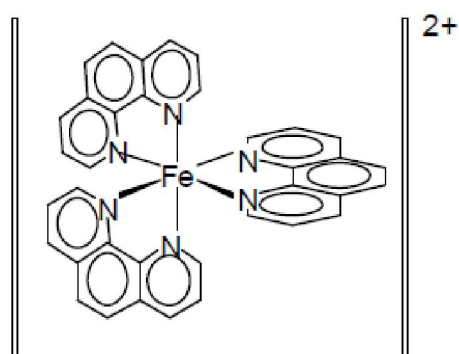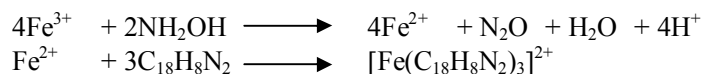
$$4Fe^{3+} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + H_2O + 4H^+$$
$$Fe^{2+} + 3C_{18}H_8N_2 \longrightarrow [Fe(C_{18}H_8N_2)_3]^{2+}$$

Figure 1. The structure of the iron-1,10-phenanthroline compound

The common aqueous forms of silica are H_4SiO_4 and $H_3SiO_4^-$ (APHA, 1997). In the presence of magnesium, it can form scale deposits in boilers and in steam turbines. Determination of silicate in water based on the reaction between silicate and ammonium molybdate in acid media to form yellow form ß-molybdosilicic acid (silicomlybdate). This complex is reduced by ascorbic acid to form heteropoly molybdous-blue complex and the absorbance was measured at 815 nm. Interference from phosphate, which forms a phosphomolybdate complex was eliminated by the oxalic acid introduced to the sample before the addition of the ascorbic acid reagent.

Linearity test

Linearity test for analysis method conducted to demonstrate the capability of the method to produce a linear relationship between the concentration of the instrument response from a series of standard solutions. Linearity of an analysis procedure can also be defined as the ability (within a given range) to generate the data analysis that is proportional to the concentration of analyte in the sample. Linearity should be determined by using a minimum of five standards whose concentration span 80 –120% of the expected concentration range.

The parameters used to indicate that relationship is linear correlation coefficient. The results may not show a significant deviation from linearity, which means the value of the correlation coefficient R> 0.99 in the working range (80-120%). In addition, the acceptance criteria of linearity was also determined from intercept where the value of the intercept does not differ much from zero, or less than 2% (McPolin, 2009).

Linearity test in Figure 2 shows the value of the coefficient of determination R^2 0.996 for Fe and 0,998 for SiO_2. It means that the correlation coefficient were 0.998 for Fe and 0,999 for SiO_2. Figure 2 also shows that the intercept were less than 2%. These data indicate that the

method of determination of Fe and SiO_2 by UV-Vis Spectrophotometry meet the criteria to guarantee the quality of the analysis data.
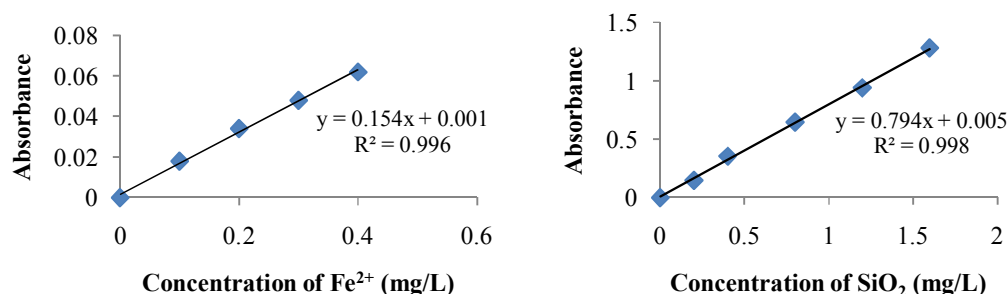

Figure 2. Calibration curve of Fe and SiO_2 standard solution

Precision test

The precision of an analytical procedure expresses the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions (APVMA, 2004). Precision may be considered at three levels: repeatability, intermediate precision and reproducibility. Parameter used to determined precision value in this paper was repeatability. Repeatability expresses the precision under the same operating conditions (samples, analyst, instrument, laboratory) over a short interval of time. Repeatability is also termed intra-assay precision (Huber, 2010). Repeatability value can be used for evaluating consistency of analyte and the difficulty of the methods. % RSD was used to determine the precision parameters criteria which criteria applied in PT Krakatau Steel was the % RSD <2% (high precision), 2-5% (moderate precision), and> 5% (low precision).

Table1. Repeatability data for test methods of Fe and SiO_2 content in water samples

	Absorbance		Concentration (mg/L)	
No	Fe	SiO_2	Fe	SiO_2
1	0.017	0.533	0.220	16.782
2	0.018	0.531	0.233	16.719
3	0.019	0.512	0.246	16.120
4	0.018	0.513	0.233	16.152
5	0.019	0.512	0.246	16.120
6	0.018	0.531	0.233	16.719
7	0.018	0.533	0.233	16.782
Mean			0.235	16.485
SD			0.00897	0.33248
%RSD			3.819	2.017

The data in Table 1 show that the % RSD value for seven repetitions in testing Fe and SiO_2 in the range 2-5% This means that both methods have moderate precision. Then, repeatability limit (*r*) can be calculated from %RSD using the equation (Haider, 2006):

$$r = 2.83 \text{ x } \%RSD$$

Thus, *r* value for testing Fe was 10.81% while for testing SiO_2 was 5.71%. *r* value were used to judged the equivalency of two test result within one laboratory where if they differ by more than the r value they shall be judged not equivalent. *r* value is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

Accuracy test

Accuracy (bias) is a measure of the difference between the expectation of the test result and the accepted reference value (true value) due to systematic method and laboratory error. The accuracy of an analytical method may be determined by any of the following ways:

1. Analyzing a sample of known concentration (for example, a control sample or certified reference material) and comparing the measured value to the true value.
2. Compare the results of the method with results from an established reference method (the uncertainty of the reference method is known).
3. If certified reference materials or control samples are not available, a blank sample matrix of interest can be spiked with a known concentration by weight or volume. The resulting mixture is assayed, and the results obtained are compared with the expected result.
4. If a blank sample matrix are not available, a standard addition method can be used. Standard addition method (spiked sample). Accuracy is calculated as the percentage of recovery by the assay of the known added amount of analyte in the sample.

Table 2. Accurcy data for test methods of Fe and SiO_2 content in water samples

No	Concentration of sample (mg/L)		Concentration of spike (mg/L)	Concentration of spiked sample (mg/L)		recovery (%)	
	Fe	SiO₂		Fe	SiO₂	Fe	SiO₂
1	0.220	16.782	1	1.090	17.821	87.00	103.90
2	0.233	16.719	1	1.116	17.600	88.30	88.10
3	0.246	16.120	1	1.103	17.254	85.70	113.40
4	0.233	16.152	1	1.155	17.222	92.20	107.00
5	0.246	16.120	1	1.142	17.128	89.60	100.80
6	0.233	16.719	1	1.090	17.695	85.70	97.60
7	0.233	16.782	1	1.103	17.726	87.00	94.40
Mean						87.93	100.74

This paper used the last method to assess accuracy by calculate the percentage recovery of spiked samples. Table 2. shows the data of accuracy assessment of testing Fe and SiO_2 in industrial water. The acceptance criteria for accuracy was determined from %recovery value, which must be in the range of 85-115%. From Table 2. it can be concluded that both method have meet the criteria with the %recovery values for Fe and SiO_2 test method are 87.93 and 100.74%, respectively.

Detection Limit

The detection limit (DL) is the smallest number analyte in a sample that can be detected which still gives significant response compared with a blank (Harmita, 2004). Several approaches for determining the detection limit are possible, depending on whether the procedure is a non-instrumental or instrumental as follow:

1. Based on visual evaluation: the detection limit is determined by the analysis f samples with known concentrations of analye and by establishing the minimum level at which the analyte can be reliably detected.
2. Based on signal-to-noise. Determination of signal-to-noise rati is performed by comparing measures signals from samples with known low concentration of analyte with those of blank samples and establishing the minimum concentration at which the analyte can be reliably detected.

3. Based on standard deviation of the response and the slope. The detection limit may be expressed as:

$$DL = 3.3\,\sigma/S$$

where σ is standard deviation of the response, S is the slope of calibration curve

4. Based on the standard deviation of the blank. Measured of magnitude of analytical background response is performed by analyzing an appropriate number of blank samples and calculating the standard deviation of these response.

5. Based on the calibration curve. A specific calibration curve should be studied using samples containing an analyte in the range of DL. The residual standard deviation of regression line or the standard deviation of y-intercept of regression lines may be used as the standard deviation (Kalra, 2011).

Table 3. Detection limit data for test methods of Fe and SiO_2 content in water samples

No	Absorbance of blank		Concentration of blank (mg/L)	
	Fe	SiO_2	Fe	SiO_2
1	0.006	0.006	0.039	0.008
2	0.005	0.004	0.032	0.005
3	0.005	0.005	0.032	0.006
4	0.004	0.004	0.026	0.005
5	0.005	0.003	0.032	0.004
6	0.003	0.005	0.019	0.006
7	0.004	0.006	0.026	0.008
Mean			0.029	0.006
SD			0.00637	0.00153
DL			0.049	0.011

This paper used method which based on standard deviation of blank to measured DL which can be calculated as:

$$DL = \bar{x} + 3\sigma$$

where $\bar{x}$ is mean of blank concentration and σ is standard deviation of the blank. The data of DL assessment is shown in Table 3. The detection limits of UV-Vis Spectrophotometer instrument used in this research were 0.049 mg/L for Fe and 0.011 mg/L for SiO_2. It means that analyte whose concentration less than DL may not be detected.

Verification parameters assessment included linearity, precision, accuracy and detection limit indicate that the method of determining the content of Fe and SiO_2 using UV-Vis Spectrophotometer according to ASTM 019 D.1068.84 and SOP.3133 QP02 have met the criteria. Therefore both methods can be used as a method for routine procedures and produce valid data in order to control the quality of the water industry in PT Krakatau Steel.

CONCLUSION AND SUGGESTION

1. The value of correlation coefficient for linearity test, %RSD for precision test, % recovery for accuracy test and limits of detection for the determination of Fe with ASTM D.1068.84 method are respectively 0.996; 3.803%; 87.94%; and 0.048 mg/L.

2. The value of correlation coefficient for linearity test, %RSD for precision test, % recovery for accuracy test and limits of detection for the determination of SiO_2 with SOP.3133 QP02 019 method are respectively 0.998; 2.014%; 100.76%; and 0,010 mg / L.

3. Parameter value of method verification indicates that the test method of Fe and SiO_2 by UV-Vis spectrophotometry meet the requirements and can be used as a routine method for testing water samples in the laboratory chemical industry PT Krakatau Steel Cilegon

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