Cyanide analysis based on complexing of CN\(^{-}\) ion and spectrophotometry method

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Abstract. Cyanide analysis based on the complexing of CN\(^{-}\) with Ni\(^{2+}\) ions by UV-Vis spectrophotometry has been performed. This study aims to obtain the maximum wavelength of cyanide-nickel absorption complexes, optimum conditions and UV-Vis spectrophotometric validation. The reaction between the green Ni\(^{2+}\) ion and the colorless CN\(^{-}\) ion occurs in the solution to form a yellow [Ni(CN)\(_{4}\)]\(^{2-}\) complex, the maximum absorption is obtained at a wavelength of 308 nm. The optimum condition of [Ni(CN)\(_{4}\)]\(^{2-}\) complex gave at pH 6 and the concentration of Ni\(^{2+}\) solution of 0.001 M at a cyanide concentration of 0.004 M, while the optimum time formed by the complex occurred in 110 minutes and the complex compound was stable for 1390 minutes (± 23 hours 10 minutes). Validation of cyanide analysis method using Ni\(^{2+}\) ion gives linear regression equation \(y = 47.446x - 0.0184\) with value \(R^2 = 0.9958\) at concentration range CN\(^{-}\) 0.0003 M to 0.008 M; LOD 0.0006 M; % RSD = 0.97%; And % recovery = 103.8%. Based on the validation results, this method can be used to determine the cyanide content using Ni\(^{2+}\) ions as complexes by UV-Vis spectrophotometry.

1. Introduction
Cyanide is a chemical compound containing cyano (─C≡N) groups [1]. There are sources of cyanide, such as fungi, bacteria, and plants [2] and its extensively found in the wastes of the refinery, coke plant, and metal plating industries [3]. Some inorganic cyanide compounds such as sodium cyanide (NaCN) and potassium cyanide (KCN) are groups of compounds having negatively charged polyatomic cyanide ions (CN\(^{-}\)). This compound is a salt of a highly toxic hydrocyanic acid. Cyanide can form complexes with cadmium, copper, nickel, silver, zinc and some other metals. The cyanide complex when dissolved will produce HCN in little or no amount at all depending on the stability of the complex. The stability of the cyanide complex varies, it depends on the central metal. Weak complexes such as the cyanide complex with zinc and cadmium will easily break down into free cyanide. The complex is like a cyanide complex with copper, nickel, and silver will be more difficult to unravel than a weak complex. Whereas powerful complexes such as cyanide complexes with gold, iron, and cobalt tend to be difficult to break down to produce free cyanide. Cyanide is most harmful substances on humans, Earth, and most aquatic life even at low concentrations [4]. Therefore, analysis of cyanide content in foods and beverages needs to be controlled. The methods used for cyanide analysis before are distillation, chromatography or Potentiometry [5], titrimetric [6], electrochemical [7,8], voltammetric [9] and fluorometric [10,11,12], while in this research was studied the optimum condition of the complex ([Ni(CN)\(_{4}\)]\(^{2-}\)) for CN\(^{-}\) analysis base on spectrophotometry method. Ni\(^{2+}\) ions with a cyanide solution may react to form a yellow tetracyanonicate (II) ([Ni(CN)\(_{4}\)]\(^{2-}\)) complex. The
color of the green Ni$^{2+}$ ion solution change to yellow after reacting with the cyanide ion to form the tetracyanonicate (II) complex ([Ni(CN)$_4$]$^{2-}$). Based on the equation of the reaction of ionizing CN ion with Ni$^{2+}$ ion can determine cyanide concentration in a sample of solution at optimum condition by UV-Vis spectrophotometry.

2. Experimental

2.1. Chemicals
Potassium cyanide (KCN), sodium hydroxide (NaOH), disodium hydrogen phosphat (Na$_2$HPO$_4$), nickel (II) chloride hexahydrate (NiCl$_2$.6H$_2$O) and hydrochloric acid (HCl) were produced by Merck. While sodium dihydrogen phosphate (NaH$_2$PO$_4$) obtained from Sigma Aldrich. The all of solution was prepared with aquades. It also used photopolymerisation with ultraviolet radiation of a wavelength of approximately 250-350 nm.

2.2. Complexing Cyanide with Ni$^{2+}$ Ion and Maximum Absorption Wavelength
The tetracanonicate (II) [Ni(CN)$_4$]$^{2-}$ complex may be prepared by mixing 2 mL of aqueous Ni$^{2+}$ 0.00025 M solution and 2 mL of a cyanide solution 0.01 M. Then, measure complex absorbence [Ni(CN)$_4$]$^{2-}$ at a wavelength of 250–800 nm with a UV-Vis Spectrophotometer. The highest absorbance at a particular wavelength is the maximum absorbance wavelength of the complex.

2.3. Cyanide Complex Optimization
The effect of pH on CN$^-$ complexing with Ni$^{2+}$ ions is done by providing 0.04M cyanide solution with various pH (4-10), 2 mL of each of these solutions was added with 2 ml of Ni$^{2+}$ (0.04 M) solution and homogenized. Furthermore each of these mixtures is measured uptake with Uvi-Visible at a wavelength of 308 nm. The maximum absorption shows the optimum pH for complex formation [Ni(CN)$_4$]$^{2-}$. While the effect of Ni$^{2+}$ ion concentration was tested by providing Ni$^{2+}$ solution with various concentration (0.00001, 0.00005, 0.0001, 0.0005, 0.001, 0.005) molar. Further, 2 mL of each of these solutions is mixed with cyanide solution (optimum pH, concentration 0.004 M). each of these mixtures was measured uptake at a wavelength of 308 nm. The highest uptake showed the optimum Ni$^{2+}$ concentration for the formation of the complex [Ni(CN)$_4$]$^{2-}$.

2.4. Determination of Complex Time and Complex Stability
2 mL cyanide solution 0.004 M at optimum pH was mixed with 2 mL of Ni$^{2+}$ ion 0.001 M solution (at optimum concentration). Then, measure absorption at maximum wavelength with UV-Vis Spectrophotometer within 0 to 180 min. While time of complex stability will be followed by the measurement of the uptake until the absorbance value decreases from the absorbance value at the optimum time. The absorbance was measured at maximum wavelength with a UV-Vis spectrophotometer [13].

2.5. Calibration Curve and Limit of Detection
2 mL of the cyanide solution (0.0003 to 0.008) molar was mixed with 2 mL of Ni$^{2+}$ 0.001 M ion solution and homogenized in separate tube. Then measure of solution absorbance at maximum wave length. Create a calibration curve between the concentration versus the absorbance value, then find the equation of the straight line. The calibration curve obtained, calculated the smallest concentration that can still be detected (limit of detection /LOD) using statistical calculations [14]. The LOD values can be calculated using the following equation:

$$\frac{SY}{X} = \sqrt{\frac{\sum(Y - Yi)^2}{n - 2}}$$
2.6. Repeatability and recovery

The 0.004 M 2 mL cyanide solution was mixed with 2 mL of Ni\textsuperscript{2+} 0.001 M solution in the reaction tube at optimum pH. Then, measure absorption at maximum wavelength with UV-Vis Spectrophotometer. Testing is done 7 times and calculate % RSD it. The percentage of standard relative deviation can be calculated using the following equation [15].

\[
LOD = 3 \frac{SY}{Slope}
\]

Whereas the recovery test was carried out by mixing 2 mL of cyanide solution (0.004, 0.0006, and 0.0009) molar with 2 mL of Ni\textsuperscript{2+} ion solution of 0.001 M and homogenized. Then measure the absorption at maximum wavelength. Next, the % recovery value is determined by the following equation:

\[
\% RSD = \frac{SD}{\bar{x}} \times 100
\]

\[
\% R = \frac{Cs}{c} \times 100\%
\]

where C is the actual concentration of cyanide and Cs is the concentration of cyanide determined by the complexation and UV-Vis method [14].

2.7. Sensor Regression Analysis Test Using SPSS Program 16

Regression analysis test was done by using statistical calculation using r\textsuperscript{2} test, f test, t test, and decision making with p-value and calculation was done by using SPSS 16 program. The hypothesis used was [16].

H\textsubscript{0} = The hypothesis states that there is no relationship between the independent variable (x) and the dependent variable (y).

H\textsubscript{1} = Hypothesis that states the relationship between independent variables (x) and the dependent variable (y).

3. Results and Discussion

3.1. Complexing Cyanide with Ni\textsuperscript{2+} Ion and Maximum Absorption Wavelength

CN\textsuperscript{-} ion solution with a solution of Ni\textsuperscript{2+} ions will react to form a complex of tetracyanonic acid (II) ([Ni(CN)\textsubscript{4}]\textsuperscript{2-}). The color of the green Ni\textsuperscript{2+} ion solution turns yellow after reacting with the CN\textsuperscript{-} ion forming the tetracyanonicate (II) complex ([Ni(CN)\textsubscript{4}]\textsuperscript{2-}). The chemical reaction equation between CN\textsuperscript{-} ions and Ni\textsuperscript{2+} ions is shown in the following:

\[
[Ni(H_2O)\textsubscript{6}]^{2+} + 4CN^- \rightarrow [Ni(CN)\textsubscript{4}]^{2-} + 6H_2O
\]

Determination of the maximum wavelength of tetrasianoniculate (II) ([Ni(CN)\textsubscript{4}]\textsuperscript{2-}) compound is aimed at obtaining an absorbency value that can provide good measurement sensitivity. The result of the determination of the maximum wavelength of tetrasianoniculate (II) ([Ni(CN)\textsubscript{4}]\textsuperscript{2-}) compound is shown in Figure 1. The three peaks observed at wavelengths 263, 284 and 308 nm are characteristic of the [Ni(CN)\textsubscript{4}]\textsuperscript{2-} complex. The results of this study are similar to the previous studies that have been reported by Lee et. al [17]. In this study, the maximum wavelength used is at 308 nm wavelength. The
selection of these maximum wavelengths is based on the peak intensity of the $[\text{Ni(CN)}_4]^{2-}$ complex which increases as the CN$^-$ ion concentration also increases. This explains the wavelengths of 263 and 284 nm, when the concentration of CN$^-$ enlarged ions will be obtained very high absorbance value, so that the absorbance value gives a poor measurement sensitivity and also not in accordance with the range of absorbance values received by Lambert-Beer's law.

3.2. Effects of pH and Ni$^{2+}$ concentration

The degree of acidity (pH) has considerable influence on the formation of the tetracyanonicate (II) complex ($[\text{Ni(CN)}_4]^{2-}$). In this research, the formation of complex $[\text{Ni(CN)}_4]^{2-}$ at varying pH is at pH 4 to pH 10. The results of pH variation effect are shown in Figure 2.

In Figure 2, it can be seen that there is a considerably drastic increase in the uptake of the $[\text{Ni(CN)}_4]^{2-}$ complexes at pH 6 to pH 7 and tends to decrease after pH 7. Based on the results of the study, the
optimum conditions of the complex \([\text{Ni(CN)}_4]^2-\) is achieved at pH 6. This means that at pH 6 complex compounds \([\text{Ni(CN)}_4]^2-\) are formed more than at other pHs. The change in pH of the solution obviously greatly influences the formation of complex compounds \([\text{Ni(CN)}_4]^2-\). At higher pH (pH above 6) the complex \((\text{Ni(CN)}_4)^2-\) solution becomes turbid as a result of precipitation of nickel hydroxide \((\text{Ni(OH)}_2)\). It is characterized by the high absorbance value shown in the resulting image of the precipitate formed, so that the resulting \([\text{Ni(CN)}_4]^2-\) (complex) compound is less than pH 6. The concentration or concentration of Nickel (II) also gives effect to the complex \([\text{Ni(CN)}_4]^2-\) measured uptake at a wavelength of 308 nm. The result of the measurement of the variation of concentration of \(\text{Ni}^{2+}\) solution is shown in curve form in Figure 3.

![Figure 3](image)

**Figure 3.** The effect of \(\text{Ni}^{2+}\) concentration to absorbance value

The optimum conditions on the concentration variation of \(\text{Ni}^{2+}\) solution occurs at a concentration of 0.001 M with an absorption value of 0.530. It shows at a concentration of 0.004 M cyanide solution to react with a solution of \(\text{Ni}^{2+}\) 0.001 M to form more complex \([\text{Ni(CN)}_4]^2-\) compounds and in the solution all \(\text{CN}^-\) ions have formed complex compounds.

3.3. Complex and Complex Stability Time

The effect of complexing time and complex stability here is to obtain optimum time when the complex \([\text{Ni(CN)}_4]^2-\) is formed and how long the compound complex remains stable. The time result is complex \((\text{Ni(CN)}_4)^2-\) and the complex stability of \([\text{Ni(CN)}_4]^2-\) can be seen in Figures 4.

![Figure 4](image)

**Figure 4.** The complexation and stability time of \([\text{Ni(CN)}_4]^2-\)
The longer time complexing the higher the absorbance value obtained. This explains the complex \([\text{Ni(CN)}_4]^{2-}\) that is formed more and more as time passes. The result of the optimum formation of the complex is in 110 minutes by giving a maximum absorbance value of 0.339, meaning that the formation of the \([\text{Ni(CN)}_4]^{2-}\) complex is best to occur in the 110th minute and the complex compound has been formed so that For the next stage of research used 110 minutes as the optimum time. At the time of complex stability the compound complex (\(\text{Ni(CN)}_4\))^{2-} is still stable for 1500 minute.

3.4. Calibration Curves and Limit of Detection (LOD)

The calibration curve made indicates the relationship between the concentration of the working solution and the absorbance value obtained from each of the concentration of the working solution. Preparation of calibration curve in this study by making seven working solutions of CN ion from a solution of CN ion concentration of 0.04 M. The concentration of CN ion working solution used as standard series is 0.0003, 0.0005, 0.0008, 0.001, 0.003, 0.005, and 0.008 M and measured at a maximum wavelength of 308 nm. The measurement results are made directly in the form of calibration curves which can be seen in Figure 5.

![Figure 5. The calibration curve cyanide](image)

The linear regression equation obtained on the above calibration curve is \(y = 47.446x - 0.0184\) with the value of the relation coefficient \((r) = 0.9958\). The value of the relation coefficient \((r)\) approaching 1 can be expressed linear relationship between the concentration of CN ion and the resulting absorption. The linearity of a method is seen from how well the relationship between absorbance \((y)\) and the concentration of \(\text{CN}^-\) ions in the calibration curve [18]. Determination of the detection limit (LOD) is obtained from the further processing of the calibration curve data that has met the analytical requirements. The detection limit (LOD) obtained from a statistical calculation of 0.0006 M. LOD values represent the lowest number of CN ion concentrations that can still be detected and detected. The LOQ value represents the lowest quantity of CN ion concentration that can still be quantitatively measured with precision (precision) and accurate (exact) accuracy [19].

3.5. Repeatability and Recovery

The precision test aims to see how closely the difference in value obtained when repeated measurements are made. This precision test is performed by measuring complex repeatability \([\text{Ni(CN)}_4]^{2-}\) which is done seven times repetition. The relative standard deviation (\% RSD) gives the condition the value generated by the coefficient of variation \(\leq 2\%\). In this research, the value of RSD is 0.97\%. This means that the precision data obtained in this study meets the given requirements, so it can be concluded that the analytical methods used have met the criteria well. The accuracy test aims to
see the proximity of the measured result to the true value. Accuracy is expressed as a percent recovery (% recovery) of added analytes. Determination of accuracy in this study using the method of simulation (spiked-placebo recovery). In the simulation method, a plurality of pure material analyte was added to the placebo (all mixed reagents used) and the mixture was analyzed and the results were compared with the standard concentrations added (actual concentration). The absorbance value obtained is then incorporated into the linear regression equation on the calibration curve to obtain the value of the analytical concentration of the measurement results. These results were compared with the actual concentrations of the analyte. The accuracy test was performed by measuring 3 variations of CN ion concentration in the range of standard series concentrations used from 0.0003 to 0.008 M to form the calibration curve. From the research results obtained the value of recovery of 103.8%. The recoverability requirement (% recovery) is in the range of 80% to 120%, so the acquisition value earned meets the requirements. Then the research data can be said to give good accuracy test results and analytical methods can work quite accurately.

3.6. Regression Analysis Test Using SPSS Program 16

Linear regression analysis has several purposes one of which to describe the phenomenon of data or cases under investigation. Regression analysis test was done by using $r^2$ test, f test, t test, and decision making with p-value. Based on Table 1, can be seen the value of coefficient of determination ($R^2$) of 0.996. The coefficient of determination is a squiggling of the value of R (0.998) that is 0.998 = 0.996 equals 99.6% which means that the concentration has an effect on the absorbance of 99.6%. While the rest (100% - 99.6% = 0.4%) is influenced by other variables beyond this regression model (error). The value of the coefficient of determination ranges from 0 to 1. The greater the value of the coefficient of determination (the closer to 1), the better the regression model obtained. This means that the influence of concentration on absorbance is stronger.

| Model | $R$ | $R^2$ | Adjusted $R^2$ | Std. Error of the Estimate |
|-------|-----|-------|-----------------|-----------------------------|
| 1     | .998a | .996  | .995           | .009787                     |
| a. Predictors: (Constant), Concentration |

ANOVA Table 2 following can be seen that the value of $F$ arithmetic amounted to $1.188 \times 10^3$, because $1.188 \times 10^3 > 6.607891$ using a significance level of 0.05 then $H_0$ rejected, so it can be concluded that the regression model obtained can be used. In addition, it can also take a decision based on the probability value (p-value) in the Sig column. If p-value $<0.05$, then $H_0$ is rejected. In the above data can be concluded that 0.000 $<0.005$ so $H_0$ rejected.

| Model | Sum of Squares | df | Mean square | $F$ | Sig. |
|-------|----------------|----|-------------|-----|------|
| 1     | Regression     | .114| 1 | .114 | 1.188E3 | .000a |
|       | Residual       | .000| 5 | .000 |       |      |
|       | Total          | .114| 6 |       |       |      |
| a. Predictors: (Constant), Concentration |
| b. Dependent Variable: Absorbance |
Table 3. show that the obtained t value of 34.468 while the value of t table obtained by 2.364624, then t arithmetic (34.468) > t table (2.364624) H0 value rejected. If H0 is rejected, then the independent variable x (concentration) has a significant contribution to the dependent variable y (absorbance).16

**Table 3.** Regression Coefficient Value Data Using SPSS Program 16.  

| Model         | Unstandardized Coefficients | Standardized Coefficients | t     | Sig. |
|---------------|-----------------------------|---------------------------|-------|------|
| (Constant)    | -.018                       |  .005                     | -3.528| .017 |
| Konsentrasi   | 47.446                      | 1.377                     | .998  | 34.468|.000 |

a. Dependent Variable: Absorban

4. Conclusions

The maximum absorption wavelength for CN- ion complexing with Ni2+ ions by UV-Vis spectrophotometry is 308 nm. At optimum conditions, this complexing is shows good accuracy, precision and longer stability. In addition, low detection limits and wide linear response suggest this method is good for CN analysis. This is also reinforced by regression model test obtained from the calibration curve using the SPSS 16 program can reject H0 and receive H1. This means that the regression moiety obtained from the calibration curve is perfectly acceptable.

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