Development of Indirect Spectrophotometric Method for Mercury Determination Based on The Formation of Iron(III)-Thiocyanate Complex

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Abstract. A new spectrophotometric method for mercury determination has been developed based on the complexation of mercury(II) in ascertained excess of thiocyanate. The remaining thiocyanate is reacted with iron(III) to form a red iron(III)-thiocyanate complex which gave maximum absorbance at 460 nm. The concentration of mercury(II) is inversely proportional to the decrease absorbance of the complex. The method was optimized to the concentrations of thiocyanate and iron(III). Selectivity of the method has also studied based on percent recovery of mercury(II) in the presence of common metal ions in the tailing waters of gold mine. Under the optimum conditions, the method showed linear correlation to mercury(II) concentration from 1-30 mg L⁻¹ with detection limit of 0.58 mg L⁻¹. The method was not interfered in the presence of all metal ions studied up to 50 mg L⁻¹, except of silver which was tolerated at 10 mg L⁻¹. The developed method has been satisfactorily applied for mercury(II) determination in synthetic and tailing waters of gold mine samples.

1. Introduction
Mercury pollution has become a global concern as its toxicity can cause severe health problems. The exposure of volatile metal mercury can induce neurological and behavior disorder, harm the kidney and thyroid, pneumonitis, which in excessive exposure led to death [1]. The wide spread of mercury contamination has been observed in several places in Indonesia which mainly generated from small-scale gold mining. Therefore, monitoring mercury in the small scale gold mining environment is important to prevent the health hazard and global environmental pollution.

Determination of mercury usually uses cold-vapour atomic absorption [2-4]. This method has high accuracy and precision in determining small amount of mercury (up to ng/L) but this method need a specific expertise in analysis and operated using expensive instrumentation. Because of those factors, spectrophotometric method for mercury determination is popularly selected and mostly developed in developing countries [5]. Spectrophotometry employing complexing agent for mercury determination has long reported and well known. The earliest method was reported employing thiocyanate to form
colorless mercuric thiocyanate complex in aqueous or 1-butanol solutions detected using ultra violet spectrophotometer at 281 nm [6]. Other spectrophotometry methods based on complexation of mercury were reported involving complexing agents of dithizone, iodide, iodide-rhodamine B, thiocyanate-rohdamine, diacetyl monoxime isonicotinoyl hydrazone (DMIH), diphenylthiocarbazone, and anthrone phenylhydrazone (APH) [5-10]. Determinations of mercury using dithizone, iodide-rhodamine B, and thiocyanate-rhodamine B were done by involving extraction of the complex with organic solvent for detection [9-10]. Whereas the use of DMIH and diphenylthiocarbazone required synthesis and condensation procedures prior to detection [5,12]. Thus, an alternative spectrophotometric method with no requirement for extraction, synthesis, and condensation procedure is required in order to develop a simple and fast analysis. Efforts for developing environmentally friendly methods for mercury determination have been reported based on the formation of tetraiodomercurate(II) and blue starch-iodine [13], which gave linearity measurement from 1-9 mgL$^{-1}$ mercury(II).

This paper reports a new spectrophotometry for mercury(II) determination based on the fact that mercury(II) ion forms colorless mercuric thiocyanate complex in the presence of excess thiocyanate [6-7], in which in the presence of iron(III) ion, the remaining thiocyanate can form a red complex of iron(III)-thiocyanate, Fe(SCN)$^{2+}$ at pH below 2 [2]. The principle of determination of mercury(II) in this experiment is based on the decrease of [Fe(SCN)$^{2+}$ absorbance which proportional to the concentration of mercury(II). The chemical parameters such as SCN$^-$ and Fe(III) concentration are optimized to increase the sensitivity of measurement. The linearity, sensitivity and validation test were also done in this experiment to assure the accuracy and precision of this new method.

2. Method

2.1. Apparatus and Reagents

All spectrophotometric measurements were carried out using single beam spectrophotometer (Spectronic-20). De-ionized water was used for preparation of all solutions. Stock solutions of mercury(II), thiocyanate, iron(III) were prepared by dissolving the appropriate amount of HgCl$_2$ (Merck), KSCN (Merck), and Fe(NO$_3$)$_3$ (Merck) respectively in de-ionized water. HNO$_3$ (Merck) was used to attain acidic condition. All chemicals and solvents used were of analytical reagent grade and working solutions were prepared by appropriate dilutions of the stock solution.

2.2. Optimization of Thiocyanate (SCN$^-$) Concentration

Thiocyanate was used as the complexing agent for mercury(II) and iron(III) ions. Thiocyanate concentration was optimized by mixing 0.2 mL of 100 mgL$^{-1}$ Hg(II) solution with 1mL of 1 M HNO$_3$ solution in 10 mL volumetric flask. Then, the solution was added with various concentration of thiocyanate solution in the range concentration of 4 to 22 mgL$^{-1}$, mixed thoroughly and add 0.58 mL of 1000 mgL$^{-1}$ Fe$^{3+}$ solution and add de-ionized water up to 10 mL. The final solution was measured with spectronic-20 at 460 nm.

2.3. Optimization of Iron(III) Concentration

Iron(II) ion was used to complex the free (remaining) thiocyanate and formed Iron(III)-thiocyanate complex used for detection. Optimization of iron(II) concentration was conducted similarly to procedure 2.2 using optimum concentration of thiocyanate; however, the concentration of iron(III) was varied from 9-58 mgL$^{-1}$.

2.4. Linearity of Mercury(II) Measurement

In order to determine the linearity of mercury(II) measurement, a series concentration of mercury(II) from 1-30 mgL$^{-1}$ were determined under optimum concentration of thiocyanate and iron(III) ions under acidic condition (pH 1) and detected spectrophotometrically at 460 nm. The absorbance of iron(III)-thiocyanate complex from all solutions with different concentration of mercury(II) were...
plotted vs the concentration of mercury(II), and examined the correlation coefficient towards linear relation.

2.5. Selectivity Test
Selectivity test was done by adding the foreign ions (Co$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and Ag$^{+}$) with various concentrations of 0, 1, 5, 10 and 50 mgL$^{-1}$ into mercury solution. Then, the absorbance of these solutions was measured by spectrophotometric detection at 460 nm and the obtained absorbance was compared to the absorbance of mercury(II) solution with no foreign ion.

2.6. Validation Test
The method was validated by applying to synthetic samples and natural sample taken from gold mine tailing soil. The tailing soil was destructed using concentrated nitric acid and diluted 100 times to suit the linear calibration. All samples were treated with the same procedure, then the results were compared to the results obtained from CV-AAS analysis.

3. Results and Discussion
Determination of mercury (II) is based on the decrease absorbance of [Fe(SCN)]$^{2+}$ complex in the presence of mercury(II). When mercury(II) is reacted with excessive thiocyanate ion (SCN$^{-}$) in acidic condition (pH < 2), some of SCN$^{-}$ ions react to Hg(II) ions forming colorless mercuric thiocyanate complex which may exist as Hg(SCN)$^+$, Hg(SCN)$_2$,$^-$, Hg(SCN)$_3^-$, and Hg(SCN)$_4^{2-}$. Under high concentration of thiocyanate ions, it is considered that the [Hg(SCN)$_4^{2-}$] complex is the predominating ion in aqueous solutions [6-7]. The remaining SCN$^{-}$ in the presence of iron(III) ion forms a red complex of iron(III) thiocyanate, [Fe(SCN)]$^{2+}$ [2,6]. The principal reaction of mercury determination in the proposed method is shown in equation (1) and (2). The absorbance of [Fe(SCN)]$^{2+}$ complex was measured using visible spectrophotometer at 460 nm. The higher concentration of Hg(II) in solution the more SCN$^{-}$ ions bound to Hg(II) ions; and thus the remaining free SCN$^{-}$ is smaller. The smaller amount of SCN$^{-}$ results smaller product of the red complex of [Fe(SCN)]$^{2+}$. The decrease of absorbance of [Fe(SCN)]$^{2+}$ is proportional to the concentration of mercury(II).

\[
\text{Hg (II) + 4SCN}^{-}\text{(excessive)} \rightarrow [\text{Hg(SCN)}]_4^{2-}\text{(colorless)} \quad (1)
\]

\[
\text{SCN}^{-}\text{(excess)} + \text{Fe}^{3+} \rightarrow [\text{Fe(SCN)}]^{2+}\text{(red)} \quad (2)
\]

Preliminary study showed that various concentration of mercury(II) under this principle of determination produced red colors with different intensity. The higher concentration of mercury(II) showed lower intensity of complex color as shown in Fig. 1.

![Figure 1. Color intensity of Fe(SCN)$^{2+}$ complex in the presence of 0-30 mgL$^{-1}$ Hg(II)](image)

3.1. Optimization of Thiocyanate (SCN$^{-}$)
The optimization of thiocyanate concentration was aimed to obtain sufficient amount of SCN$^{-}$ to complex with Hg(II) and Fe(III) ions. The concentration of SCN$^{-}$ was optimized in the range from 4 to 22 mgL$^{-1}$ and the results are shown in Fig. 2. Based on Fig. 2, higher concentration of SCN$^{-}$ produce higher amount of [Fe(SCN)]$^{2+}$ complex shown by increasing of absorbance. The absorbance increased up to 12 mgL$^{-1}$ and relatively stable for further addition (22 mgL$^{-1}$). In this experiment, 15 mgL$^{-1}$ thiocyanate was selected as optimum condition and used for further measurements.
3.2. Optimisation of Iron(III) Concentration
The optimisation of iron(III) concentration was carried out in order to obtain sufficient concentration for complexing the free thiocyanate. The influence of iron(III) concentration to complex with remaining SCN\(^{-}\) to form \([\text{Fe(SCN)}]\)^{2+} red complex is illustrated in Fig. 3, in which the higher concentration of Fe\(^{3+}\) produced higher intensity of red complex \([\text{Fe(SCN)}]\)^{2+} and subsequently resulted higher absorbance. In this research, iron(III) concentration of 40 mgL\(^{-1}\) which gave stable and acceptable intensity was selected for reproducible measurements and sensitivity reasons.

3.3. Linearity of mercury(II) measurement
Under the optimum conditions outlined above, using concentrations of 15 mgL\(^{-1}\) thiocyanate and 40 mgL\(^{-1}\) iron(III)), the method was found to give two linear calibrations for mercury(II) concentration (Fig. 4) with first linear range from 1–10 mgL\(^{-1}\) (\(y = -0.013x + 0.393\)) with coefficient determination, \(R^2 = 0.998\), and second linear range from 10-30 mgL\(^{-1}\) (\(y = -0.013x + 0.393\)) with \(R^2\) of 0.992. The detection limit of this method determined from the mean of the blank with three times standard deviation was 0.96 mgL\(^{-1}\) (\(n = 10\)).
3.4. Selection of measurement

The selectivity of the proposed was examined by monitoring the influence of foreign ions commonly present in tailing gold mine, such as Co$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and Ag$^{+}$ on the measurement of mercury(II). The effect of these ions were determined by measuring the absorbance of mercury(II) solution in the absence and in the presence of those foreign ions as shown in Fig. 5. As depicted in Fig. 5, the presence of Co$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ ions up to 50 mgL$^{-1}$ did not significantly interfere the measurement of mercury(II). However, the method only tolerated the presence of Ag$^{+}$ up to 10 mgL$^{-1}$. This is because silver(I) ion reacted with thiocyanate forming silver thiocyanate, Ag(SCN), precipitation with low constant solubility product ($K_{sp}$AgSCN $= 1.0 \times 10^{-12}$) [5].

3.5. Method Validation

In order to validate the proposed method, it was applied to determine concentration of mercury(II) in synthetic samples and natural samples of soil tailing waste obtained from small scale gold mining using standard addition method. In this method, three different concentrations of mercury(II) were added separately to three synthetic and tailing samples, and then the recoveries of mercury(II) in the sample after addition of the mercury(II) standards were determined using the proposed method. The method showed very good recoveries for synthetic samples with average percent recoveries of 102.48% as depicted in Table 1.
Table 1. Validity test using synthetic samples.

| Mercury(II) (mgL\(^{-1}\)) | Measured mercury(II) (mgL\(^{-1}\)) | Recovery (%) |
|-----------------------------|--------------------------------------|--------------|
| 1                           | 1.00                                 | 100.00±1.79  |
| 5                           | 5.27                                 | 105.41±1.80  |
| 10                          | 10.20                                | 102.03±2.30  |

Average recovery 102.48±1.37

Validity test for the proposed method was applied to tailing water from small scale gold mining with 100 times dilution (without addition of mercury(II) standard) resulting concentration of 3.85 mgL\(^{-1}\) (Table 2); thus it gave original concentration of 385 mgL\(^{-1}\). Using standard addition technique the validity of the method was determined by the percent recoveries of the sample after the addition of three different concentration of mercury(II) standards. The recoveries of the three standard additions are displayed in Table 2 depicting that the proposed method showed excellent recoveries with average percentage of 105.26.

Table 2. Recoveries of mercury(II) from tailing water by standard addition technique.

| Sample* | Added Mercury(II) (mgL\(^{-1}\)) | Measured mercury(II) (mgL\(^{-1}\)) | Recovery (%) |
|---------|----------------------------------|-------------------------------------|--------------|
| Sample  | 0                                | 3.85 mgL\(^{-1}\)                  | -            |
| Sample  | 1                                | 5.05 mgL\(^{-1}\)                  | 105.13±0.18  |
| Sample  | 2                                | 6.24 mgL\(^{-1}\)                  | 108.00±1.88  |
| Sample  | 3                                | 6.95 mgL\(^{-1}\)                  | 102.65±1.95  |

Average recovery 105.26±1.87

*Tailing water with 100 dilution factor.

4. Conclusion
The spectrophotometric method outlined above allows simple and sensitive method for determination of mercury(II) concentration. Based on the validation test, this method also showed very good accuracy and precision shown by the high recoveries of close to 100 % with low standard deviations. This result suggests that the method mentioned above is prospective to be used for monitoring of mercury(II) concentration in water and waste water samples.

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