

A Catalytic Spectrophotometric Method for the Analytical Determination of Trace Amounts of Mercury (II)

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Abstract

A catalytic method has been developed for the determination of microgram amounts of mercury (II) based on its catalytic effect on the rate of a ligand substitution reaction. The reaction studied involved the substitution of cyanide in hexacyanoferrate (II) by resacetophenone benzoic acid hydrazone (2', 4'- dihydroxy propiophenone benzoic acid hydrazone) and the reaction was monitored spectrophotometrically. Satisfactory results were obtained for the determination of mercury (II) in the range 0.1086-0.9774 µg/ml. The relative standard deviation was less than 2.1%. The method detection limit and limit of quantification was found to be 0.041 µg/ml and 0.083 µg/ml respectively (n=7). The correlation coefficient for the determination was found to be 0.9989. The effect of foreign ions on the determination was studied.

Keywords: Mercury (II) Determination; Catalytic Method; Spectrophotometry.

1. Introduction

Mercury is highly toxic element and it can be easily absorbed by the animals and human beings [1]. Due to its high toxic nature, the determination of trace amounts of mercury in water samples is of great importance. Numerous catalytic methods [2, 3] for the determination of trace amounts of metals have been reported in the literature. Only few systems have been reported which involve ligand exchange reactions, e.g., hexacyanoferrate (II) is known [4, 5] to exchange cyanide ligands with chromogenic organic ligands. Many methods [6-14] for the determination of mercury (II) reported in the literature are very expensive and employ complicated procedure. In this article, the authors report a simple catalytic spectrophotometric method for the determination of trace amounts of mercury (II). It was observed by the authors that, the colourless resacetophenone hydrazone (RBAH) reacts with yellow $K_4Fe(CN)_6$ solution in appropriate buffer medium giving a reddish brown colored solution. The structure of RBAH is shown in Figure 1.

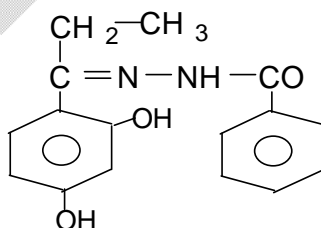


Figure 1: Structural formula of RBAH.

The development of the color was extremely slow; it requires about 24 hours to attain the maximum intensity. The addition of small amounts of mercury (II) considerably accelerates the development of colour. No such colour was observed when the metal ion was added independently to $K_4Fe(CN)_6$ or RBAH, hence the colour formation was due to the ligand exchange reaction between $K_4Fe(CN)_6$ and RBAH in the presence of mercury (II).

The reddish brown solution in the presence of mercury (II) at pH 3 showed maximum absorbance at 430 nm. At this wavelength both $K_4Fe(CN)_6$ and RBAH solutions showed negligible absorbance. Therefore a catalytic method for the determination of mercury (II) at 430 nm has been developed. Above facts are similar to that reported by Phull and Nigam [15].

2. Methods

2.1 Reagents

All the reagents were analytical grade obtained from Merck. Double distilled water was used for all the experiments. Mercurous chloride solution and potassium ferrocyanide solutions are prepared by dissolving appropriate amounts of respective compounds in double distilled water. RBAH solution was prepared by dissolving appropriate amount of RBAH in dimethylformamide. Buffer solution of pH 1.0 – 3.0 was prepared by mixing appropriate quantities of 0.1M hydrochloric acid and 0.2M sodium acetate and that of pH 4.0 – 7.0 was prepared by mixing suitable quantities of 0.2M acetic acid and 0.2M sodium acetate.

2.2 Apparatus

Absorbance measurements were made on an ELICO UV-Visible Spectrophotometer SL-164. An ELICO Digital pH meter C-212 was used for pH measurements.

3. Results and Discussion

3.1 Procedure

Suitable aliquots of buffer solution, RBAH solution, Hg (II) solution and distilled water were taken in conical flask. An aliquot of ferrocyanide solution was added from the pipette into the conical flask. A stopwatch was started when the pipette is half-empty. A known volume of the reaction mixture was withdrawn from the conical flask and absorbance was measured at known intervals of time (5 minutes) at 430 nm. The initial rates were calculated from absorbance-time curves [16].

3.2 Optimization of reaction conditions

3.2.1 pH

The change of initial rate with pH is shown in the Figure 2. The rate was maximum at pH 3. The decrease in rate at higher pH may be due to the shortage of protons needed to regenerate the catalytic species and or due to the decrease in the concentration of Hg^{2+} as a result of hydrolytic precipitation as the hydroxide. The rate is reduced at low pH values because of protonation of $\text{Fe}(\text{CN})_6^{-4}$. Therefore, pH 3 was chosen for the determination of mercury (II).

3.2.2 RBAH concentration

With the optimum pH fixed at 3, ferrocyanide concentration and mercury (II) concentration at $4 \times 10^{-3} \text{M}$ and $1 \times 10^{-6} \text{M}$ respectively, the concentration of RBAH was varied from 0.2×10^{-5} to $1.6 \times 10^{-5} \text{M}$. The linear plot of initial rate Vs RBAH is shown in the Figure 3. Keeping in view the fact that, the reaction hardly occurs at lower RBAH concentrations and higher concentrations are not advisable because of the limited solubility of the reagent in the reaction medium, a concentration of $1.0 \times 10^{-5} \text{M}$ was fixed for further studies.

3.2.3 Ferrocyanide concentration

With the other conditions as before, the concentration of ferrocyanide was varied between 0.4×10^{-3} to $6.0 \times 10^{-3} \text{M}$. The linear plot of initial rate vs ferrocyanide concentration is shown in the Figure 4. At lower ferrocyanide concentrations the reaction does not occur, whereas at higher concentrations, forward rate is inversely proportional to the concentration of cyanide ion (15). A concentration of $4 \times 10^{-3} \text{M}$ was fixed for subsequent studies.

3.3 Determination of Hg^{2+}

Different aliquots of buffer solution of pH 3, RBAH solution of concentration $1 \times 10^{-4} \text{M}$, a known aliquot of mercury solution of concentration $2 \times 10^{-5} \text{M}$ and requisite volume of distilled water were taken in a glass stoppered conical flask, stirred well and kept in a thermostat at $27 \pm 1^\circ \text{C}$. Known aliquot of the thermostated $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution of concentration $4 \times 10^{-2} \text{M}$ was added to the conical

flask. A stop watch was started when the pipette delivering $K_4[Fe(CN)_6]$ solution was half empty. A known aliquot of the reaction mixture was withdrawn from the conical flask and absorbance was measured at known intervals of time at 430 nm against a blank containing a mixture of a buffer solution of pH 3, RBAH and $K_4[Fe(CN)_6]$ solutions. The initial rates were calculated from absorbance-time curves [16].

3.4 Method validation

3.4.1 Linear range and sensitivity

Plot of absorbance Vs concentration was linear in the range 0.08 to 0.72 $\mu\text{g/ml}$ and is shown in the Figure 5. The absorbance at shorter and longer times also gave linear relationships, 30 minutes was found to be optimum for the determination. The least square calibration equation was $A = 7.1977 C + 1.3472$ (A is absorbance and C is concentration in $\mu\text{g mL}^{-1}$) which was of the straight-line equation form $Y = mX + c$ and has a regression coefficient 0.9989.

3.4.2 Selectivity

The proposed method was found to be highly selective in a solution of pH 3 at 430 nm. The effect of foreign cations and anions on the determination was studied and the tolerance limits were established; the results are presented in the Table 1.

3.4.3 Accuracy and precision

The reproducibility of the proposed method was tested by performing replicate determinations. The results given in Table 2 reveal the excellent intermediate precision (%RSD < 1.90) and accuracy (%RE \leq 2.50) of the results.

3.4.4 Robustness and ruggedness

To check the ruggedness, analysis was performed by three different chemists; and on three different spectrophotometers by the same chemist. The robustness and the ruggedness were checked at three different mercury (II) levels. The intermediate precision, expressed as percent RSD, which is a measure of robustness and ruggedness was within the acceptable limits as shown in the Table 3.

3.5 Application to the real samples

The proposed method was applied for the determination of Hg (II) in several samples. The samples were spiked with several known amounts of Hg (II). The results reported as the average values from seven sample measurements are shown in the Table 4. These results showed the applicability of the method in various types of environmental water samples.

4. Conclusion

The proposed method is simple, highly reproducible, sensitive and selective for the determination of trace amounts of mercury (II). A notable advantage of this method is that the Hg (II) determination is free from interference of almost all cations and anions found in the water samples.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

LKR and VS supervised the project and preparation of manuscript. ARGP did the actual work, prepared the manuscript and communicated to the journal.

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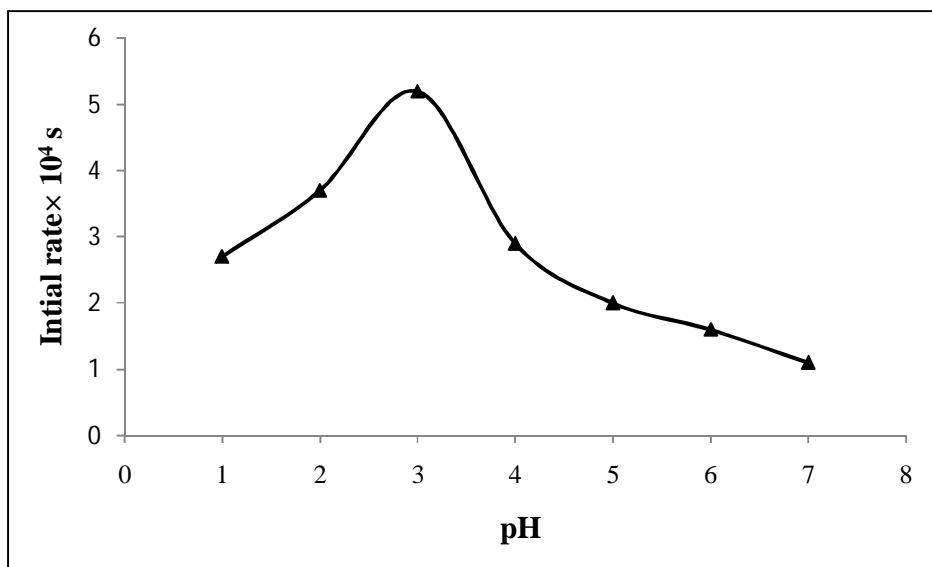


Figure 2: Effect of pH on initial rate.

$[K_4Fe(CN)_6] = 4 \times 10^{-3}M$; $[RBAH] = 1 \times 10^{-5}M$; $[Hg(II)] = 1 \times 10^{-6}M$; $\lambda_{max} = 430$ nm.

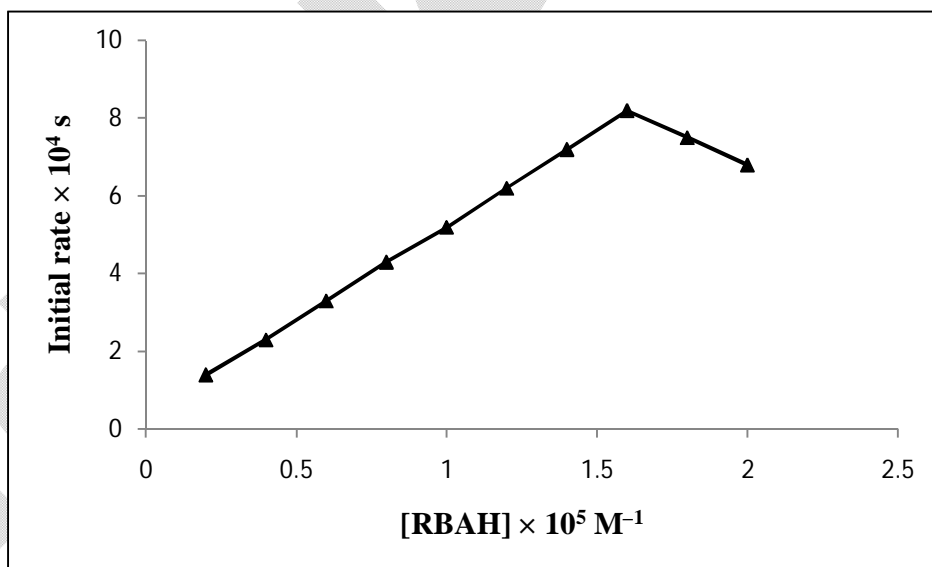


Figure 3: Effect of RBAH concentration on initial rate.

$[K_4Fe(CN)_6] = 4 \times 10^{-3}M$; $[Hg(II)] = 1 \times 10^{-6}M$; $pH = 3$; $\lambda_{max} = 430$ nm.

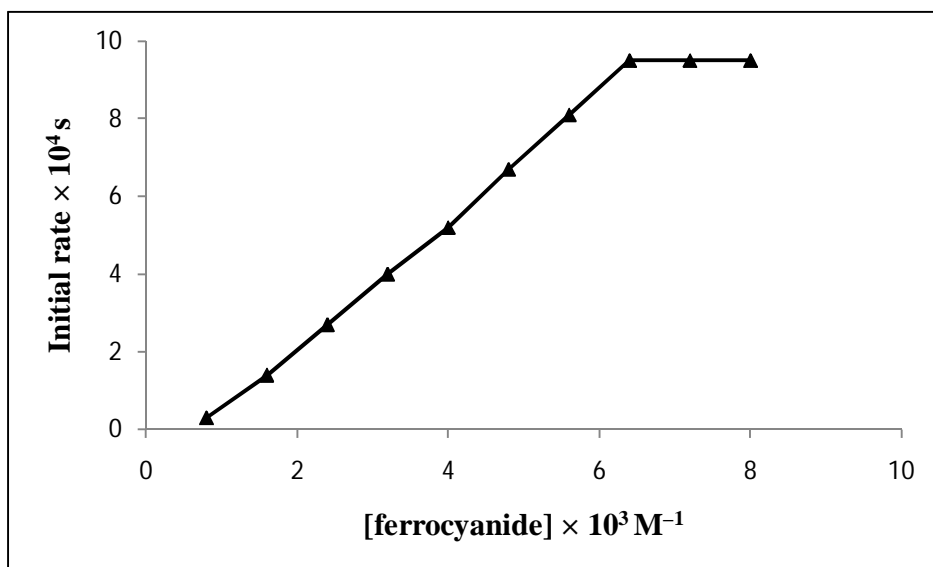


Figure 4: Effect of ferrocyanide concentration on initial rate.

[RBAH] = 1×10^{-5} M; [Hg(II)] = 1×10^{-6} M; pH = 3; λ_{\max} = 430 nm.

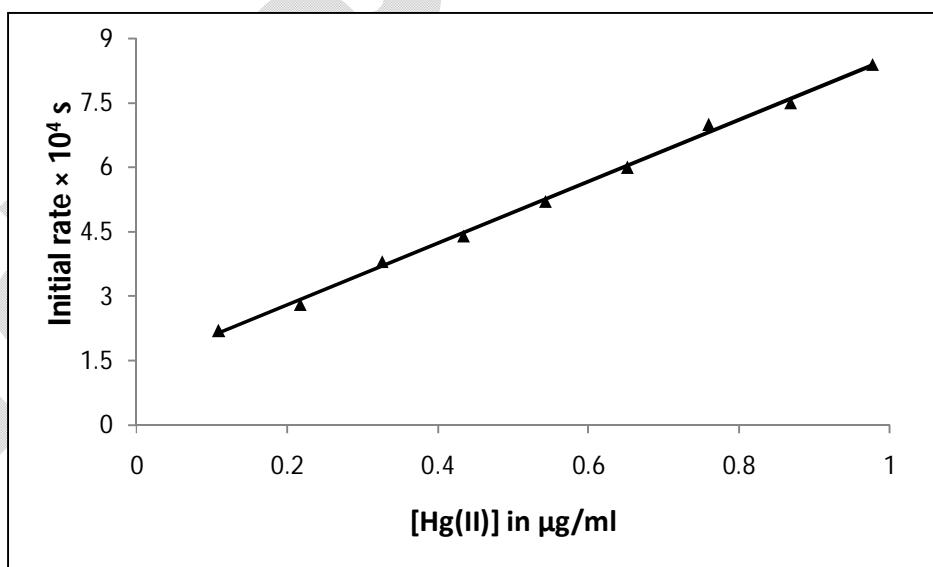


Figure 5: Determination mercury (II).

[K₄Fe(CN)₆] = 4×10^{-3} M; [RBAH] = 1×10^{-5} M; pH = 3; λ_{\max} = 430 nm.

Table 1: Effect of foreign ions on the determination of mercury (II); [Hg(II)] = 0.543 µg/ml.

Foreign ion	Tolerance limit* (µg/ml)
Oxalate	2.963
Nitrate	0.416
Sulphate	1.211
Tartrate	2.457
Phosphate	1.216
Fluoride	1.121
chloride	1.218
Bromide	9.409
Iodide	1.113
Calcium	13.273
Magnesium	11.273
Cadmium	7.562
Tungsten	10.821
Zinc	5.618
Copper	3.825
Nickel	1.727
Palladium	1.822
Lead	11.712
Barium	7.218
Tellurium	9.125
Platinum	12.120

* Average of seven determinations.

Table 2: Accuracy and precision.

Added µg/ml	Precision and Accuracy		
	Found ^a µg/ml	RSD %	Recovery ^b %
0.200	0.205±0.157	1.827	102.500
0.400	0.409 ± 0.114	1.335	102.250
0.600	0.611±0.073	0.856	101.830

^aThe tabulated value of t at 95% confidence level is 2.26; RSD. Relative standard deviation; ^bRecovery = 100% + [(Found – Added) / Added] x 100%.

Table 3: Robustness and ruggedness.

[Hg(II)] studied $\mu\text{g mL}^{-1}$	Robustness (RSD %)	Ruggedness (RSD %)	
	Reaction time ($n = 3$)*	Inter analysts ($n = 3$)	Inter instruments ($n = 3$)
0.200	1.634	1.992	2.021
0.400	1.421	1.002	1.274
0.600	1.120	1.335	0.997

* The stop clock was started after 2 min, 3 min and 4 min of the addition of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution in to the reaction mixture.

Table 4: Results of mercury (II) determination in spiked tap water.

Sample	Added ($\mu\text{g/ml}$)	Found ($\mu\text{g/ml}$)	SE $\mu\text{g/ml}$	Recovery %
Tap water	0.600	0.611 ± 0.073	0.030	101.830
	0.400	0.409 ± 0.114	0.046	102.250
	0.200	0.205 ± 0.157	0.063	102.500

RE = relative error; SE = standard error.