



SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF Hg (II) USING THE REACTION INVOLVING POTASSIUM HEXACYANOFERRATE AND DMF

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ABSTRACT: The reaction involving Potassium hexacyanoferrate (II) and the solvent DMF is spectrophotometrically monitored in the presence of buffer solution of pH 3. The addition of Hg(II) catalyzed the reaction which resulted in the development of a spectrophotometric method for the determination of Hg(II) ion in microgram quantities. The interaction between the reactants gave an orange red colored species in the pH range 1-6. The maximum absorption was observed in a buffer solution of pH 3 at the wavelength of maximum absorbance at 410 nm. The effect of time, various organic solvents on the maximum color development were studied and observed that 30 minutes time after mixing the components and the DMF solvent are found to be the most suitable. The effect of DMF solvent on the intensity of color indicated that a 40% v/v DMF used in the method is optimal. Beer's law for the spectrophotometric determination of Hg (II) was obeyed in the range 0.2µg/ ml to 1.6µg/ ml (20ng/ ml to 160ng/ ml). The molar absorptivity and Sandell sensitivity are calculated as $8.0 \times 10^4 \text{ lit.mol}^{-1}.\text{cm}^{-1}$ and 0.002507 µg/ ml respectively. The effect of various diverse ions in the determination is studied. The proposed procedure for Hg (II) determination finally agreed favorably well with the kinetic method developed.

Key words: Spectrophotometry, dimethyl formamide (DMF), Potassium hexacyanoferrate ($\text{K}_4\text{Fe}(\text{CN})_6$), Mercury(II).

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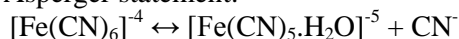
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INTRODUCTION

Potassium hexacyanoferrate (II) in aqueous solution is known to undergo dissociation at elevated temperature or under the influence of UV light. The dissociation reaction is slow but is catalysed considerably by Hg(II) ions (Asperger S.,1952) A survey of chemical literature has revealed that the reaction between $\text{K}_4\text{Fe}(\text{CN})_6$ and several organic aromatic compounds including sulpha drugs such as Sulphanil amide, Sulphamethoxazol and their condensed products are catalyzed by metal ions such as Hg(II).

These observations have resulted in the subsequent spectrophotometric quantitative determination of not only the organic compounds, (Krishna Dutta et al.1972, Madhu Phull. et al.1981, Madhu Phull Bajaj et al. 1981, Mallikharjuna Rao K. et al.1988, Faiyaz H.M. et al. 2004) the drugs and their condensed derivatives but also the Hg(II) ions (Ramachar T. et al.2012, Ramachar T. et al.2012,2014, 2016). In the present study the authors have successfully attempted to evolve a method for the spectrophotometric determination of Hg (II) alone without using the organic compounds or the drugs. The advantage of the proposed method is that the use of costly organic substances and drugs can be avoided. The results obtained are found to be in good agreement with the methods reported in literature and even with the kinetic initial rate method.

The studies are carried out in the presence of the DMF solvent in buffer solution. The results can be explained by the assumption that hexacyanoferrate (II) ion is undergoing decomposition in aqueous solution to aquapentacyanide ion as supported by Asperger statement.



However it is not possible to describe the observed absorbance exclusively due to aquapentacyanide ion since ferrocyanide ion too absorbs at the same wavelength. The increase in absorbance observed can be attributed to the fact that the decomposition is rapid in the presence of DMF or Hg(II) ion. Therefore the color reaction is explained to explore the possibility of developing a quantitative method for the spectrophotometric determination of Hg(II). The systematic behavior of the aqueous solutions of hexacyanoferrate in the presence of a suitable buffer solution, DMF and Hg(II) ions revealed that the study can be conveniently exploited for a method for the determination of Hg(II) ions. The results obtained are presented in this communication. The optimal conditions for the detailed study are carried out as follows.

EXPERIMENTAL

Apparatus, Reagents and Solutions

Apparatus: A Systronics Spectrophotometer Model-106 with wavelength range 300-900 nm is used for absorbance measurements. A toluene Hg thermostat is used for maintaining the temperature of the reaction mixture constant. pH measurements are made using an Elico LI-10 digital pH meter.

Reagents and Solutions: $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution is prepared by dissolving 4.221 gram of AR sample in distilled water and diluted to 100 ml to get a stock solution of 0.1M. Hg(II) solution is prepared by dissolving 0.2715 gram of mercury(II) Chloride in distilled water and diluted to 100 ml to get a 0.01M solution. Buffer solutions are prepared by adopting the standard procedures (Vogel A.I. 1951) mixing suitable quantities of the components concerned.

RESULTS AND DISCUSSION

(i) **Absorption Spectra:** The absorption spectra of different test solutions namely

A: 4 ml of buffer solution of pH 3 + 5 ml water + 1 ml of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (7×10^{-2} M),

B: 4 ml of buffer solution of pH 3 + 4 ml water + 1 ml of Hg(II) (5×10^{-6} M) + 1 ml of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (7×10^{-2} M), **C:** 4

ml of buffer solution of pH 3 + 3 ml water + 2 ml of DMF + 1 ml of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (7×10^{-2} M) and **D:** 4 ml of buffer solution of pH 3 + 2 ml water + 2 ml of DMF + 1 ml of Hg(II) (5×10^{-6} M) + 1 ml of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (7×10^{-2} M) (Total volume of each solution is kept at 10 ml) are recorded using buffer solution as a blank in the wavelength range 380 – 600 nm 30 minutes after the components of the test solutions are mixed.

It is observed from the absorption spectra obtained that the wavelength of the maximum absorption (λ_{max}) in each case is at 410-420 nm. Further it is also observed that there is not much difference in the shape of the absorption curves except that the absorbance values corresponding to the maximum wavelength is different in each case. Thus for all further absorbance measurements, wavelength 410 nm is fixed.

ii.) Effect of Time: With a view to know the stability of the color formed and the minimum time it takes for full color formation. The effect of time is carried out and the absorbance values of the test solution are recorded at an interval of 10 minutes each. It is noticed that complete color development occurred at 30 minutes after mixing the components and thereafter there was no appreciable change in the absorbance values.

iii.) Effect of different solvents: The absorbance values of the test solutions are recorded at 10 minutes and 30 minutes after the components are mixed in presence of different solvents (40% v/v) against buffer solution as a blank with a view to know the efficacy of each solvent in the present investigations and the results obtained are shown in Table-1.

Table-1: Solvents and absorbance

4 ml of Buffer Solution + 4 ml 40% v/v solvent + 1 ml of Hg(II) (5×10^{-6} M) + 1 ml of Fe(CN)₆ (7×10^{-2} M). Total volume = 10 ml. $\lambda_{\max} = 410$ nm

Solvent	Absorbance at	
	10 min	30 min
Water (78.0)	0.02	0.04
DMF (36.7)	0.11	0.72
DMSO (46.7)	0.03	0.06
Methanol(32.7)	0.05	0.18
Dioxane (2.2)	0.07	0.56
Acetonitrile(57.7)	0.04	0.10

DMF : Di methyl Formamide, DMSO: Di methyl Sulphoxide.

The values shown in the brackets in the above table 1 are the dielectric constants of the solvents. The results in Table1 indicate that absorbance is considerably high in DMF and next in Dioxane. There appears to be a relation between the absorbance value and the dielectric constant of the solvent. This suggests that polarity of the solvent is not responsible for the observed results. Thus DMF is chosen as the solvent for further studies.

iii.) Effect of percentage of DMF solvent: The various volume percentages of DMF are added to the test solution and the results obtained are recorded in Table-2.

Table-2: Effect of volume percentage of DMF

Test solution: 4 ml buffer solution (pH 3) + (4-x) ml water + x ml DMF + 1 ml of Hg (II) (5×10^{-6} M) + 1 ml K₄[Fe (CN)₆] (7×10^{-2} M) Total volume = 10 ml. $\lambda_{\max} = 410$ nm

Vol of DMF (x)	%DMF (v/v)	Absorbance at	
		10 Min	30 Min
1	10	0.02	0.18
2	20	0.08	0.37
3	30	0.20	0.54
4	40	0.31	0.73
5	50	0.31	0.73

The results in Table-2 suggest that a 40% (v/v) of DMF solvent is enough for maximum absorbance and so is fixed for further studies.

iv.) Effect of pH of buffer solution: To arrive at optimum pH for further studies, the absorbance of the test solution is recorded in buffer solutions of pH 1-6 and the results are presented in Table-3.

Table-3: Effect of pH of buffer solution

Test solution: 4 ml buffer solution + 2 ml water + 2 ml DMF + 1 ml of Hg (II) (5×10^{-6} M), + 1 ml K₄[Fe (CN)₆] (7×10^{-2} M) Total volume = 10 ml. $\lambda_{\max} = 410$ nm

pH	Absorbance at	
	10 Min	30 Min
1	0.04	0.21
2	0.07	0.46
3	0.09	0.70
4	0.06	0.43
5	0.03	0.14
6	0.01	0.09

From the data in Table-3, it is clear that the absorbance is maximum with buffer solution of pH 3, so pH 3 buffer solution is fixed for studies.

v.)Effect of K₄[Fe(CN)₆] Concentration: The effect of concentration of K₄[Fe(CN)₆] on the absorbance values of the test solution is studied to arrive at optimum condition and the data obtained is presented in Table-4.

Table-4: Effect of $K_4[Fe(CN)_6]$ concentration

Test solution: 4 ml buffer solution (pH 3) + (1.5-x) ml water + 4 ml DMF +0.5 ml of Hg(II) ($1 \times 10^{-5}M$) + x ml $K_4[Fe(CN)_6]$ ($4 \times 10^{-2}M$) Total volume = 10 ml. $\lambda_{max} = 410$ nm

$K_4Fe(CN)_6 \times 10^3$ M	Absorbance at	
	10 Min	30 Min
1.0	0.11	0.26
2.0	0.23	0.58
3.0	0.28	0.72
4.0	0.31	0.77
5.0	0.32	0.79
6.0	0.33	0.79

It is seen from the results shown in Table-4 that a minimum concentration of 5×10^{-3} M of $K_4[Fe(CN)_6]$ is required for complete color development. Hence $5 \times 10^{-3}M$ concentration of $K_4[Fe(CN)_6]$ can be fixed for further studies.

Recommended Procedure for Hg (II) determination

4 ml of buffer solution of pH3 , (1.5-x) ml of water ,4 ml of DMF, different aliquots(x) of Hg(II) (5×10^{-6} M) and 0.5 ml of $K_4[Fe(CN)_6]$ are mixed and resulting total volume is made upto 10 ml in various 10 ml standard flasks. The absorbance of these solutions is recorded at 410 nm against buffer solution as blank. The data obtained is presented in Table-5.

Table-5: Hg Absorbance

Test solution: 4 ml buffer solution (pH 3) + (1.5-x) ml water + 4 ml DMF + x ml of Hg (II) ($5 \times 10^{-6}M$) + 0.5 ml $K_4[Fe(CN)_6]$ Total volume = 10 ml. $\lambda_{max} = 410$ nm

Amount of Hg(II) in $\mu g/ml$	Absorbance at	
	10 min	30 min
0.2	0.04	0.08
0.4	0.08	0.16
0.6	0.12	0.24
0.8	0.16	0.32
1.0	0.20	0.40
1.2	0.24	0.48
1.4	0.27	0.56
1.6	0.30	0.63
1.8	0.31	0.65
2.0	0.32	0.66

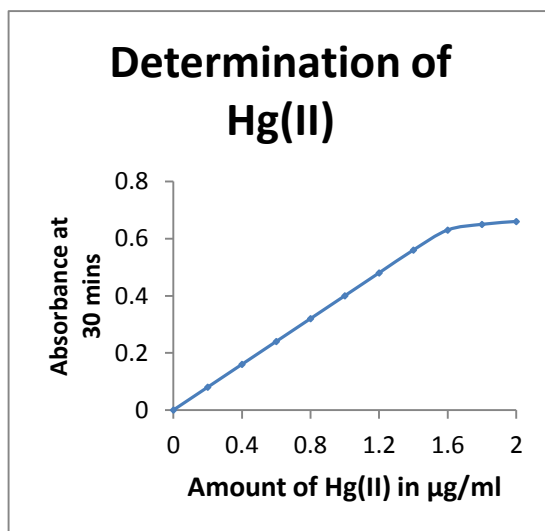


Fig-1: Calibration curve – Obedience of Beer-Lambert’s Law

The data in Table-5 and Fig-1 indicate a proportionate linear increase in the absorbance with the increase in the concentration of Hg(II). This suggests the suitability of the method for the spectrophotometric determination of Hg(II) in the range 0.2 $\mu\text{g/ml}$ to 1.6 $\mu\text{g/ml}$ or 20 ng/ml to 160 ng/ml. The molar absorptivity and sandell sensitivity of the method are $8.0 \times 10^4 \text{ lit.mol}^{-1}.\text{cm}^{-1}$ and 0.002507 $\mu\text{g/ml}$ respectively.

Kinetic Procedure

The reaction is monitored spectrophotometrically at 27⁰ C and the initial rate is calculated from the absorbance-time data. The absorbance – time curves are constructed with the experimental results and the initial rate is computed using the plane mirror method. The absorbance of the test solutions containing the known aliquots of Hg(II) ion are recorded at 410 nm at different time intervals and the initial rate is computed by the plane mirror method. The data is presented in table-6 and Fig-2.

Table-6: Hg(II) Kinetic rates

Amount of Hg(II) in ng/ ml	Initial Rate $\times 10^3 \text{ sec}^{-1}$
20	0.70
40	1.40
60	2.10
80	2.80
100	3.50
120	4.20
140	4.90
160	5.50
180	5.80
200	6.00

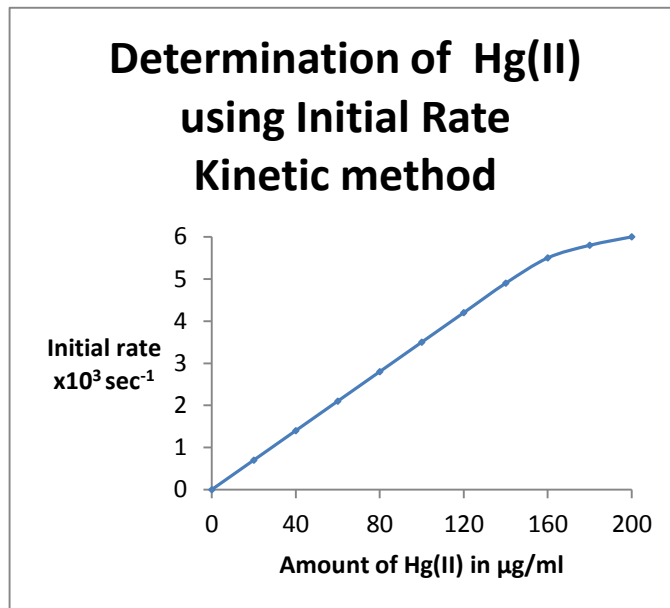


Fig-2: Rate of Hg(II) kinetic method

The data in Table-6 and Fig-2 show that the variation between the amount of Hg(II) and the initial rate is proportionate and the curve obtained is linear in the range 20 ng/ml to 160 ng/ml or 0.2 $\mu\text{g/ml}$ to 1.6 $\mu\text{g/ml}$. Hence, this confirms the suitability of the initial rate kinetic procedure for the quantitative spectrophotometric determination of Hg(II) in the above mentioned range.

Study of Thermodynamic parameters: The thermodynamic parameters such as ΔE^* , ΔH^* , ΔS^* and ΔG^* at three different temperatures with different initial kinetic rates are evaluated and the results obtained are presented in Table-7.

Table-7: Thermodynamic Parametrs

Temp (°C)	Initial Rate $\times 10^3$ (sec) ⁻¹	ΔE^* KCal/mole	ΔH^* KCal/mole	ΔS^* Cal/mole/deg	ΔG^* KCal/mole
29.9	2.3	14.12	13.5	-20.40	19.72
30.4	2.9				
30.9	5.0				

(v.) **Effect of Foreign ions:** To understand the determination of Hg(II) ions in presence of the other foreign ions, the effect of various diverse ions is studied on the color reaction. A deviation of $\pm 2\%$ in the absorbance is taken as the tolerance limit of the added diverse ion. The results are shown in Table-8.

Table-8: Effect of Foreign Ions

Foreign ions	Tolerance limit in $\mu\text{g/ml}$	Foreign ions	Tolerance limit in $\mu\text{g/ml}$
Ba ⁺²	>20000	Cl ⁻	>20000
Mg ⁺²	600	SO ₄ ⁻²	>20000
Al ⁺³	180	Br ⁻	>10000
Cu ⁺²	6.4	NO ₃ ⁻	>10000
Co ⁺³	3.0	PO ₄ ⁻³	>10000
Ni ⁺²	3.0	C ₂ O ₄ ⁻²	>200
Pb ⁺²	2.0	SCN ⁻	>200
Fe ⁺²	1.3	F ⁻	0.95
Cd ⁺²	1.4	I ⁻	0.50

ACKNOWLEDGEMENTS

The authors is grateful to the authorities of G.Pulla Reddy Engineering College (Autonomous), Kurnool for their constant encouragement. One of the authors (TR) expresses his sincere and heartfelt gratitude to Dr. G. Abdul Huq for his keen interest in the progress of this work.

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ISSN : 0976-4550

INTERNATIONAL JOURNAL OF APPLIED BIOLOGY AND PHARMACEUTICAL TECHNOLOGY



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