International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Online International Journal Available at http://www.cibtech.org/jcs.htm
2012 Vol. 2 (3) July-September pp.1-6/Vijaya et al.

Research Article

A CATALYTIC SPECTROPHOTOMETRIC METHOD FOR THE ANALYTICAL DETERMINATION OF TRACE AMOUNTS OF MERCURY (II) USING 2-HNAINH

D. Vijaya Kumari[1], K. Vasudha[2], V. Sai Sathyavathi[3] and *R Kishore Kumar [1]
[1]*Department of Chemistry, S.V. Arts College (Degree and PG Courses), Tirupati (A.P) India - 517502*
[2]*Department of Chemistry, S.P.W. Degree and PG College, Tirupati (A.P) India - 517502*
[3]*Department of Chemistry, Anna Adarsh College for Women, Chennai - 600082*
**Author for Correspondence*

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 2-HNAINH (2-hydroxy 1-napthaldehyde isonicotinoyl hydrazone) and the reaction was monitored spectrophotometrically. The reaction is readily catalyzed by the mercury (II) ions in the pH range 2-5.The orange red solution formed in this study exhibits maximum absorbance at 470 nm in pH-3.The optimum concentration of $K_4Fe(CN)_6$ and 2-HNAINH are found to be $2x10^{-4}$M $2x10^{-3}$ M and Satisfactory results were obtained for the determination of mercury (II) in the range 0.004-0.048 µg/ml. The effect of different parameters such as pH, temperature, concentration of Hg (II) ions on the initial rate of the reaction is studied. The effect of foreign ions on the determination was studied. The results which are obtained quite satisfactory. This method promises to become a sensitive spectrophotometric method for the determination of mercury (II).

Key Words: *Mercury (II), Catalytic Method, 2HNAINH, Spectrophotometer*

INTRODUCTION

Mercury is highly toxic element and it can be easily absorbed by the animals and human beings (O'Neil, 1995). Due to its high toxic nature, the determination of trace amounts of mercury in water samples is of great importance. Numerous catalytic methods (Petkovic *et al.*, 2007; Qin and Guohua, 2003) 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 (Gadia *et al., 1978*; Mohan 2007) to exchange cyanide ligands with chromomeric organic ligands. Many methods (Fischer, 1993 and Huang, 2002) (Fischer *et al.,* 1993; Huang *et al.*, 2002; Qin *et al.*, 2003; Gadia *et al.*, 1978; Mohan *et al.*, 2007; Fischer *et al.,* 1993; Huang *et al.,* 2002; Svarc *et al.*, 2006; Hosseini *et al.*, 2005; Padmaja *et al.*,1994; Rajesh *et al.*, 2008 and Resano *et al.*, 2005) for the determination of mercury (II) reported in the literature are very expensive and employ complicated procedure. Kinetic methods are as sensitive as luminescence and activation analysis methods. (Shafawi *et al.*, 1999) The thermal decomposition of hexacyano ferrate (II) is a slow reversible process. Baudish (1927) and Ilmori (1927) proposed that aqueous solution of potassium hexacyanoferrate (II) decomposes slowly to aqua pentacyanoferrate (II) and cyanide ions in the presence of ultraviolet light. The pentacyanoaquo complex produced reacts with aromatic nitroso compounds and produces colored complexes. Salicyladehyde isonicotinoyl hydrazone was used for the spectrophotometric determination of gallium and indium at pH 6-6.5. In the present method a simple catalytic spectrophotometric method for the determination of trace amounts of mercury (II). It was observed by the authors that, thermal decomposition of hexacyano ferrate (II) is a slow process. When 2-HNAINH is added to aqueous solution of $K_4Fe(CN)_6$ in weakly acidic medium faint orange red colour solution is formed. It took about 24 hours for the development of deep orange red colour but addition of small amounts of mercury (II) accelerated the development of deep orange red colour. No such colour was observed when the metal ion was added independently to K_4Fe

$(CN)_6$ or 2-HNAINH, hence the colour formation was due to the ligand exchange reaction between $K_4Fe(CN)_6$ and 2-HNAINH in the presence of mercury (II).

MATERIALS AND METHODS

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. 2-HNAINH solution was prepared by dissolving appropriate amount of 2-HNAINH 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.

Apparatus

Absorbance measurements were made on SHIMADZU 240 UV-Visible Spectrophotometer SL-164. A Metrohm Digital pH meter SWISS make was used for pH measurements.

RESULTS AND DISCUSSION

Procedure

Suitable aliquots of buffer solution, 2-HNAINH 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 470 nm.

Kinetic Procedure Initials Rate Method

Initials rate method described in present method the stock solutions involved in the study are thermo stated at the desired temperature for about half an hour. Then appropriate quantities are mixed in the sequence-buffer (40%), dimethyl formamide (20%) as solubuliser, mercury (II), 2HNAINH and $K_4Fe\ (CN)_6$ solutions. A stop watch is started when the pipette delivering $K_4Fe\ (CN)_6$ in to the reaction mixture is half empty. The solution is shaken well and immediately transferred in to the cuvette .The cuvette is placed in the temperature controlled compartment of the spectrophotometer and the absorbance measured at 470 nm at definite intervals of time against hexacyanoferrate (II) solution as the blank .The initial rates are calculated from the absorbance –time curve using the plane mirror method proposed by Latashaw.

Absorption Spectra

The absorption spectra of the following solutions against buffer blank are recorded to arrive at an optimum wavelength for the absorbance measurements.

Solution A:

4ml of buffer solution (pH3) + 1ml of DMF + 1ml of 2HNAINH ($2x10^{-3}$M) + distilled water = 10ml.

Solution B:

4 ml of buffer solution (pH 3) + 1 ml of DMF+0.5 ml of $K_4Fe\ (CN)_6$ ($2x10^{-3}$M) +distilled water =10ml.

Solution C:

4 ml buffer solution (pH 3) +1 ml of DMF + 1ml of 2HNAINH ($2x10^{-3}$M) +0.5 ml of $K_4Fe\ (CN)_6$ ($2x10^{-3}$ M) + distilled water = 10 ml.

The spectra of solution A, B and C thus obtained are presented in the Figure 1. It is clear from the figure that the solution C has absorption maximum at 470 nm. At this wavelength solution A has at least zero absorbance and solution B has negligible absorbance. Hence λ max is fixed at 470 nm and potassium ferrocyanate (II) chosen the blank for further studies.

Effect of pH

The Experimental solutions containing hexacyanoferrate (II) ($2x10^{-3}$M), 2HNAINH ($2x10^{-4}$M) and mercury (II) ($1x10^{-7}$M) are prepared using the buffer solutions of desired pH. 20% (v/v) DMF is maintained. The initial rates are determined at 30^0c. The results suggest that the initial rate is maximum buffer solution of pH 3. The low rate in pH s 1 and 2 may due to the protanation and the decrease at higher pH s may be due to the depletion in the concentration of Hg^{2+} because of the hydrolytic precipation as hydroxide. pH 3 is chosen for further studies. The results are presented in Figure 1.

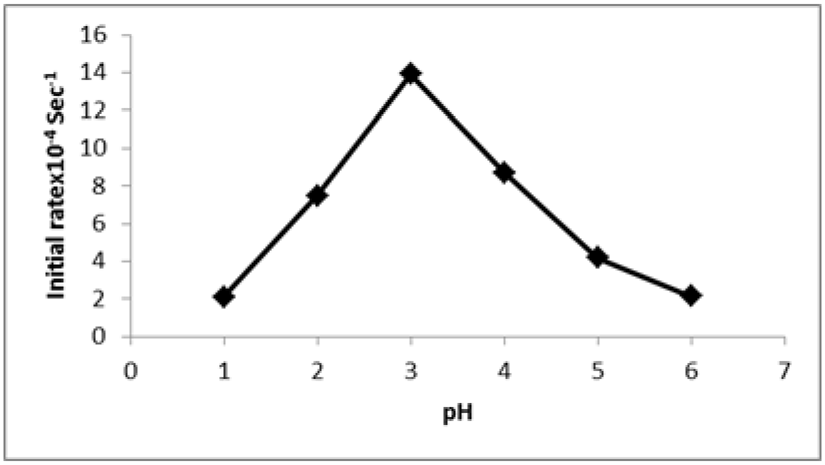

Figure 1: Effect of pH

Effect of 2 HNAINH Concentrations

The ferrocyanide concentration and mercury (II) concentration fixed at 2×10^{-3}M and 1×10^{-7} M respectively and the concentration of 2HNAINH were varied from 1×10^{-4} to7×10^{-4} M. It is clear from the graph that the plot is linear up to $4x10^{-4}$ M and then remains unchanged. Hence an optimum concentration of 2HNAINH is fixed at $2x10^{-4}$ M for further studies. The linear plot of initial rate Vs 2 HNAINH in Figure 2.

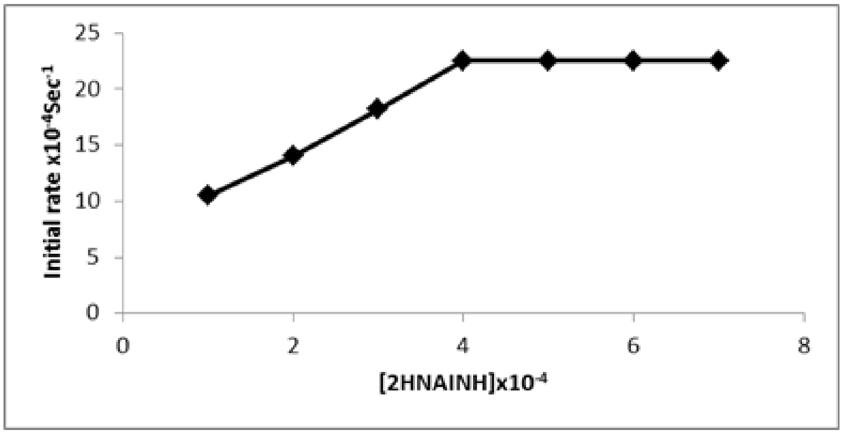

Figure 2: Effect reagent concentrations (2HNAINH)

Effect of Ferrocyanide Concentration

Experimental solutions are prepared in a set of 10 ml standard flasks using buffer solution of pH 3 and maintaining 20% DMF. The concentrations of 2HNAINH and smercury (II) are fixed at $2x10^{-4}$ M and $1x10^{-7}$M respectively. To this known aliquots of potassium hexacyanoferrate (II) are added and the initial rates determined at 30^0c .The results are presented in the Figure 3. A graph is drawn between the initial rate and the concentration of K4Fe $(CN)_6$ .The figure suggest that the rate increases rapidly up to $4x10^{-3}$ M ,but at higher concentrations rate increases is slow and does not become constant. Therefore further experiments are carried at optimum concentrations of $2x10^{-3}$M.

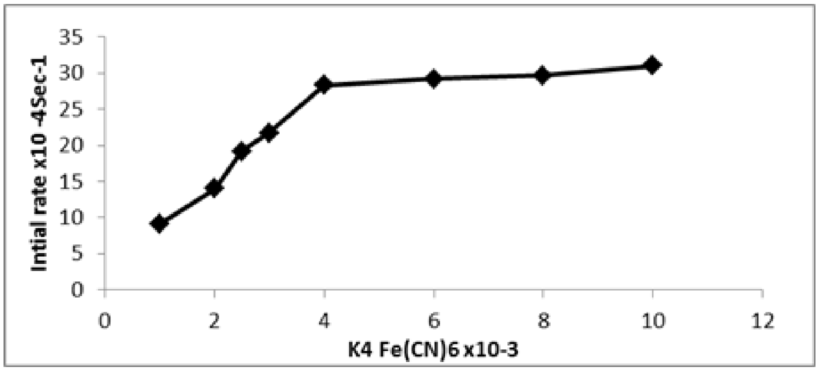

Figure 3: Effect of Ferrocyanide concentration

Determination of Hg2+

Fixing the pH at 3 and maintaining the concentrations of $K_4Fe(CN)_6$ and 2HNAINH at 2x10 $^{-3}$ and 2x10^{-4}M respectively, the concentration of $HgCl_2$ solution is varied in the range 0.2x10^{-7}M to 2.8x10^{-7} M. The reaction is followed at 30 ^{0}c and the initial rates calculated. The results are presented in Table 1. A calibration curve drawn between the amounts of mercury added and the initial rate is shown in Figure 4.

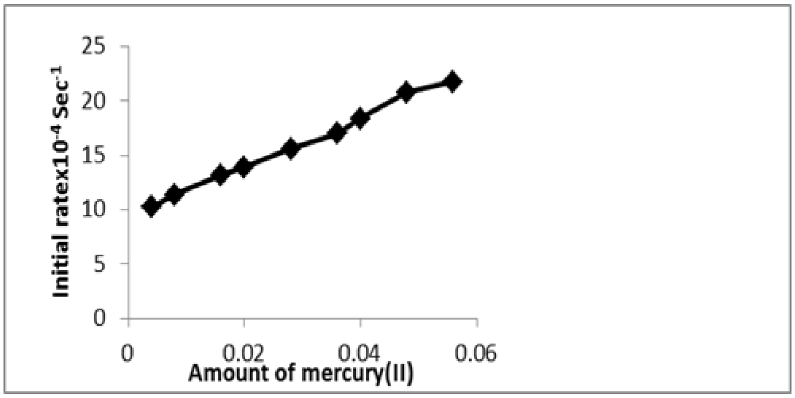

Figure 4: Effect of mercury (II) µg ml-1

This curve suggests that mercury (II) can be determined in the range (0.004 - 0.048 µg.ml^{-1}).

Table 1: The amount of mercury (II) determination

Amount of Mercury (II)	Initial Ratex10 ^{4} Sec^{-1}
0.004	10.20
0.008	11.40
0.016	13.20
0.020	13.90
0.028	15.60
0.036	17.00
0.040	18.41
0.048	20.80
0.056	21.80

The intercept obtained by exploration the straight line gives the rate of the unanalysed reaction. The decline in the rate at higher concentrations of mercury (II) may be due to the formation of a binary *adduct [Fe (CN)* $_{6.HgCl\ 2}$*], as the adduct is known to decrease the rate of the forward reaction. The existence of a similar complex between Fe* $(CN)_6^{-4}$ *and Hg* $(CN)_2$ *is reported by Beck et al.*

Effect of Temperature

The concentrations of $K_4Fe\ (CN)_6$, 2HNAINH and $HgCL_2$ are fixed at $2x10^{-3}M$,$2x10\ ^{-4}$ M and $1x10^{-7}$M respectively and the initial rates determined at 20^0c , 25^0c, 30^0c and 35^0C. Higher temperatures are not attempted for fear of probable decomposition of the orange red complex. The results indicate that the initial rate increases with temperature. As the reaction process at a measurable rate 30^0c.Further studies are carried out at the laboratory temperature 30^0c.

Effect of Foreign Ions

In order to explore the analytical applicability of this method, the effect of diverse ions substances on the determination of mercury (II) is studied. Keeping the pH at 3 and the concentrations of $K_4Fe(CN)_6$, 2HNAINH and $HgCl_2$ at $2x10^{-3}$, $2x10^{-4}$ and $1x10^{-7}$M respectively, the effect of diverse substances on the initial rate is studied at 30 ^{0}C .The error in the initial rate of the order of ± 2% is taken as the tolerance limit. The results are presented in the Table 2.

Table 2: Effect of diverse of substances, Amount of Mercury (II) =0.02 µg .ml-1

Diverse Substances	Tolereance Limit µg .ml $^{-1}$
Nitrate	20
Sulphate	16
Phosphate	12
Chloride	10
Thicyanate	10
Thiosulphate	08
Fluoride	01
Magnesium(II)	12
Calcium(II)	08
Barium(II)	08
Cobalt(II)	03
Aluminium(II)	02
Nickel(II)	01

CONCLUSIONS

During the course of investigation it is observed that hexacyanoferrate (II) forms an orange red complex with 2HNAINH in buffer solution of pH 3 which is a slow reaction. This reaction is due to the replacement of cyanide in hexacyanoferrate (II) by isonicotinoyl hydrazones of carbonyl compounds and this is readily catalysed by the mercury (II) ions in the pH range 2-5.

ACKNOWLEDGEMENTS

My sincere thanks to Retd Professor K. Lakshmi Naryana, Dept Chemistry, S.V. University, A.P, India, for his able guidance.

REFERENCES

Baudisch (1929). *O Ber* (62) 2706.

Fischer R, Rapsomankis S and Andreae MO (1993). Determination of methylmercury in fish samples using GC/AA and sodium tetraethylborate derivatization. *Analytical Chemistry* **65** 763-766.

Gadia MK and Mehra MC (1978). Analytical reactions of substituted cyanoferrates 2. Pentacyanoamminoferrate (II) in catalytic spectrophotometric determination of sub parts per million amounts of Ag+, Au3+, and Hg2+ in solution. *Micro Chemical Journal* **23** 278-284.

Hosseini MS and Moghaddam HH (2005). Sensitized extraction spectrophotometric determination of Hg (II) with dithizone after its flotation as ion-associate using iodide and ferroin. *Talanta* **67** 555-559.

Huang W and Zhang S (2002). Determination of mercury at a dithizone-modified glassy carbonelectrode by anodic stripping voltametry**.** *Analytical Sciences* **18** 187-189.

Ilmori Z (1927). *Anorganic Chemistery* 167-157.

Mohan Reddy KPRR, Govind Chowdary P, Krishna Reddy V and Raveendra Reddy P (2007). Catalytic-kinetic determination of silver (I) using hexacyanoferrate (II) and 2, 4, 6-tripyridyl-1, 3, 5-triazine (TPTZ). *Annali Di Chimica* **97**(11-12) 1207-1215.

O'Neil P (1995). Chapman and Hall. *Mercury in Environmental Chemistry* 2nd edition (London).

Padmaja P, Balasubramanian PN and Ramakrishna TV (1994). Chemical enhancement method for the determination of mercury by spectrophotometry after iodide extraction. *Talanta* **41** 255-260.

Petkovic BB, Simonovic RM and Micic RJ (2007). Determination of ultramicroquantities of Au (III) by its catalytic effect on 4-hydroxyl coumarone oxidation with potassium permanganate. *Journal of Analytical Chemistry* **62**(7) 697-700.

Qin W, Guohua C, Jinhu Y and Bin D (2003). Catalytic kinetic spectrophotometric determination of trace amounts of silver in triton x-100 micellar medium. *Analytical Letters* **36**(6) 627-640.

Rajesh N and Gurulakshmanan G (2008). Solid phase extraction and spectrophotometric determination of mercury by adsorption of its diphenylthiocarbazone complex on an alumina column. *Spectrochimica Acta, Part-A* **69**(2) 391-394.

Resano M, Gelaude I, Dams R and Vanhaecke F (2005). Solid sampling electrothermal vaporization inductively coupled plasmamass spectrometry for the direct determination of Hg in different materials using isotope dilution with a gaseous phase for calibration. *Spectrochimica Acta, Part-B, Atomic Spectroscopy* **60**(3) 319-326.

Schintzer G, Soubelet A and Chafey C (1995). Comparison of open and closed focused microwave digestions in view of total mercury determination by cold vapour atomic absorption spectrometry. *Mikrochimica Acta* **119** 199-209.

Shafawi A, Ebdon L, Foulkes M, Stockwell P and Corns W (1999). Determination of total mercury in hydrocarbons and natural gas condensates by Atomic Fluorescence Spectroscopy. *Analyst* **124**(2) 185-189.

Svarc-Gajic J, Suturovic Z, Marjanovic N and Kravic S (2006). Determination of mercury by chronopotentiometric stripping analysis using glassy carbon vessel as a working electrode. *Electroanalysis* **18**(8) 513-516.