

Kinetic Estimation Of Lead In Micro Amounts In Environment Through The Catalytic Effect On Ligand Substitution Reaction Between Hexacyanoferrate(II) And 1,10 Phenanthroline

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ABSTRACT

The Lead has been known to catalyse the reaction between hexacyano ferrate (II) and phenanthroline in the concentration range 2.5×10^{-7} - 2.5×10^{-8} M. A catalytic Kinetic Method based on fixed time procedure has been developed for estimation of lead by spectrophotometrically following the progress of the reaction at 528 nm. The reaction conditions chosen for the progress of the reaction were: Ionic strength $I = 0.15$ M (KNO_3), Temp = $25.0 \pm 0.1^\circ C$ and pH = 3.0 ± 0.02 . On the basis of experimental results for the catalyzed reaction the following rate expressions was derived:-

$$\frac{d[Fe(CN)_6phen^{3-}]}{dt} = k'[Fe(CN)_6]^{4-} + k_2'[Pb^{+2}]$$

In this equation k' is the rate constant for uncatalysed path and k is composite rate constant. The detection limit is evaluated by standard procedure and is found to be $3.0 \times 10^{-7} M$ in $[Pb^{+2}]$.

Keywords: lead, phenanthroline, hexacyanoferrate, kinetic.

INTRODUCTION

Day-to-day exposure to lead may occur from old lead piping or paint, soil or dust from industry using lead and from vehicle exhaust where leaded petrol has been used. Workers in certain industries might also be exposed to lead at what might, over time, become dangerous levels. Lead is a cumulative poison which affects the central nervous system. It can also increase the risk of premature birth, reduce birth weight, induce learning difficulties, inhibit growth, damage the kidneys, cause weakness in the joints, affect the memory, damage the male reproductive system, cause abortions and is potentially carcinogenic.

Analysis methods of lead comprise of colourmetry, X-ray fluorescence, Raman spectroscopy and isotopic scanning [1-3]. All these above stated methods are very costly and during the past few years, many enhanced and novel analytical methods for determining of Mercury (II) [4-9,13,14], and few other metals like Ruthenium [10], cobalt (II), Nickel (II) [11], copper [12], have been developed but only a few complicated methods are present for lead.

Thus, the use of lead catalysed ligand substitution reaction of hexacyano ferrate (II) can be used for the trace determination of lead using kinetic catalytic Method (KCM) since of it has many advantages over the known conventional method [12,15]. Many of these reactions are of the oxidative type of Reactions [16-24]. The instances of ligand substitution reactions of hexacyanoferrate are scanty [25-29], due to its less labile nature. In several instances the catalytic action of lead (II) involving slow redox reaction [21-24] are being used to develop KCMs for determining and analysis of lead (II). These techniques are less costly and extremely sensitive. The main advantage and usefulness of KCM is the fact that only one instrument i.e. a simple spectrophotometer is required in this technique.

In this paper, we have tried to develop a new sensitive Kinetic method for estimation of lead (II) based on its catalytic activity on the ligand substitution reaction between hexacyanoferrate (II) and phenanthroline and hexacyanoferrate (II), under optimum conditions of reaction. This method can be accepted widely due to its high selectivity, more precision, higher sensitivity and above all its cost effectiveness.

EXPERIMENTAL

Chemicals, solvents and solutions

All analytical grade reagents were utilized in our experiment. Double distilled water was taken to make all of the experimental solutions. Stock solutions of $2.5 \times 10^{-2} M$ Lead(II) chloride, $2.5 \times 10^{-2} M$ Phenanthroline and $2.5 \times 10^{-2} M$ potassium hexacyanoferrate (II) were made after calculating the required amount from the analytical grade reagents in the double distilled water. Hexacyanoferrate(II) solution was kept in brown coloured bottles to prevent photo - decomposition reaction of the complex compound. Everyday just before the setting of the experiment the solution of hexacyanoferrate (II) and lead(II) were

diluted as per need. With the aid of phthalate sodium hydroxide buffer, the pH of the reaction mixture was maintained at 3.0 ± 0.02 , as given in literature [30]. Ionic strength was maintained with the help of potassium nitrate at 0.1 M.

Instrumental

The pH measurement were made on a digital pH meter of Sio-global. All the reactant solutions were equilibrated at 25°C by keeping them inside environmental chamber in order to maintain the desired temperature. Genesis Model No. 10UV was used to record the spectra of the reaction. All glassware were steamed before use. Certified "A" grade volumetric apparatus were used throughout the study. Quartz cuvettes were cleaned by dipping them in 1:1 nitric acid for 15 minutes to remove all the traces of impurities. The standard BDH buffers were used for standardization of pH meter.

Kinetic measurements

For the attainment of thermal equilibrium all the reactant solutions were kept in the environmental chamber at $25.0 \pm 0.1^\circ\text{C}$ for approximately 30 minutes. Then, 2ml of 2.5×10^{-4} mol L^{-1} of phenanthroline solution, 2ml of phthalate buffer solution ($\text{pH} = 3.0 \pm 0.02$) and 2ml of 3.0×10^{-7} – 3.0×10^{-8} M solutions of lead chloride were pipette in sequence into a 25 ml graduated flask and then above mixture was mixed with 2 ml of 2.5×10^{-2} M hexacyanoferrate (II) finally to start the reaction. The solution was transferred to a 10mm quartz cuvette after shaking, to record the absorbance. The absorbance was recorded after 15, 20, and 25 min of the reaction, and The data so obtained were utilized to plot the calibration curves for the determinations of Lead(II).

RESULTS AND DISCUSSION

A the fixed time procedure was adopted to record the Absorbance A_t after 15, 20 and 25min, after mixing of the reagents. Hexacyanoferrate (II) was taken in sufficiently excess amount and phenanthroline was taken in non-rate-limiting excess quantity then a graph was Plotted of the A_t values versus the concentration of Pb^{+2} , which was found to be linear.

Fig. 1 is The graph of A_t versus (Pb^{+2}) and

Table 1 is of Absorbance at fixed time (A_t) as a Function of $[\text{Pb}^{+2}]$

The linear regression co-relating the A_t values to the Pb^{+2} concentration between 2.5×10^{-7} – 2.5×10^{-8} M are represented by Eqns. 1-3.

$$A_{15} = 3.7 \times 10^5 [\text{Pb}^{+2}] + 0.07 \quad (1)$$

$$A_{20} = 3.2 \times 10^5 [\text{Pb}^{+2}] + 0.112 \quad (2)$$

$$A_{25} = 2.8 \times 10^5 [\text{Pb}^{+2}] + 0.137 \quad (3)$$

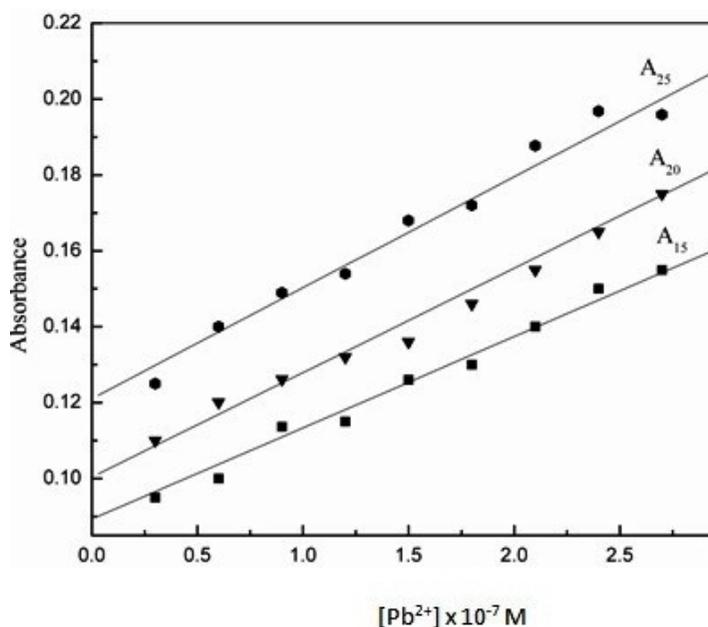


Fig. 1: Determination of $[\text{Pb}^{+2}]$ by Calibration Curves

Under conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 7.5 \times 10^{-3} \text{ M}$, $[\text{phen}] = 4.5 \times 10^{-4} \text{ M}$, $\text{pH} = 3.0 \pm 0.02$, $I = 0.15 \text{ M} (\text{KNO}_3)$, $\text{Temp} = 25.0 \pm 0.1^\circ \text{C}$.

TABLE 1. Absorbance at fixed time (A_t) as a Function of $[\text{Pb}^{+2}]$

$[\text{Pb}^{+2}] \times 10^{-7}$	A_{15}	A_{20}	A_{25}
0.25	0.095	0.115	0.130
0.50	0.105	0.125	0.145
0.80	0.115	0.130	0.150
1.10	0.125	0.135	0.155
1.40	0.135	0.140	0.165
1.70	0.145	0.155	0.175
2.15	0.155	0.160	0.185
2.30	0.165	0.170	0.190
2.60	0.175	0.175	0.205
3.00	0.185	0.190	0.215

Under Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 7.5 \times 10^{-3} \text{ M}$, $[\text{phen}] = 4.5 \times 10^{-4} \text{ M}$, $\text{pH} = 3.0 \pm 0.02$, $I = 0.15 \text{ M} (\text{KNO}_3)$ and $\text{temp} = 25.0 \pm 0.1^\circ \text{C}$

The relationship at a higher concentration of $[\text{Pb}^{+2}]$ is very complex. The rate equation for this ligand substitution reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Phen}]$ in presence of a non-rate limiting excess of $[\text{Phen}]$ and a micro amount of lead (II) is expressed in accordance to Eqn. 4.

Rate =

$$\frac{d[\text{Fe}(\text{CN})_5\text{phen}^{3-}]}{dt} = \frac{k'[\text{Fe}(\text{CN})_6]^{4-} + k_2K[\text{Fe}(\text{CN})_6]^{4-}[\text{Pb}^{+2}][\text{H}_2\text{O}]}{1 + Kk_2K[\text{Fe}(\text{CN})_6]^{4-}} \quad (4)$$

The first term tells us about the rate of the uncatalysed reaction, the second term denotes the catalysed reaction, that shows a variable order dependence and the trend of leveling of the reaction rate at higher concentration of $[\text{Fe}(\text{CN})_6]^{4-}$.

When hexacyanoferrate (II) is taken in a relatively large amount the rate can be written as –

$$\frac{d[\text{Fe}(\text{CN})_5\text{phen}^{3-}]}{dt} = k'[\text{Fe}(\text{CN})_6]^{4-} + k_2'[\text{Pb}^{+2}] \quad (5)$$

In this equation k' represents an experimental rate constant for uncatalysed reaction and k_2' is built up of several terms that have been derived from the mechanism of the reaction. Eqn. (5) shows that a linear relationship exists between the concentration of Lead (II) and the initial rate of the reaction. This relationship has been found to be quite accurate as far as the present study is concerned (Figure1). It should be remembered that, the ratio of the rate of the catalysed reaction sequence to that of the uncatalysed reaction sequence must be high. Therefore, it ought to be kept in mind that $[\text{Fe}(\text{CN})_6]^{4-}$ concentration should be high enough for the catalytic pathway to be fast, but not very high so that the rate of the uncatalysed reaction becomes considerable when compared with the catalysed reaction.

The values of Absorbance changes for a little more or less reaction duration also form a linear relationship but has more % of error. As evident from the Table 2. Table 2 is for Determination of Lead and the error Computation.

The % errors related to calibration curves for A_{20} and A_{25} are higher than that for A_{15} . This takes place since A_{15} is a closer measure of the initial rate in comparison to A_{20} or A_{25} . Though sometimes a smaller 'fixed time' like of 10 minutes or even less than this can be taken but in these cases the absorbance change is smaller and their calculation, can lead to bigger % errors. Hence the time chosen by us of 15 minutes gives us convenient and adequate absorbance changes. The first calibration curve (A_{15}) versus $[\text{Pb}]^{+2}$ is therefore, recommended for to determine Lead in trace amounts in this study. This fixed time of fifteen minutes (A_{15}) allows us to take approximately 30 determinations per hour. Table 2 has shown that the determination of Lead (II) from all the taken analytes are very reasonable for monitoring the applications in the environmental.

TABLE 2. Determination of Lead and the error Computation

1520x	IJRAR- International Journal of Research and Analytical Reviews	Research Paper
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$[\text{Pb}^{+2}] \times 10^7$ M taken	$[\text{Pb}^{+2}] \times 10^7$ M Found	A_{15} % Error	$[\text{Pb}^{+2}] \times 10^7$ M Found	A_{20} % Error	$[\text{Pb}^{+2}] \times 10^7$ M Found	A_{25} % Error
0.30	0.31	+3.3	0.32	+6.6	0.27	-10.0
0.50	0.49	-2.0	0.48	-4.0	0.52	+4.0
0.80	0.85	+6.2	0.79	-1.2	0.82	+2.5
1.10	1.15	+4.5	1.12	+1.8	1.13	+2.6
1.40	1.42	+1.4	1.38	-1.4	1.44	+2.8
1.70	1.74	-2.3	1.72	+1.1	1.68	-1.1
2.15	2.12	-1.3	2.17	+1.3	2.14	-0.4
2.30	2.27	-1.3	2.32	+0.8	2.34	+1.7
2.60	2.62	-0.7	2.58	+0.7	2.65	+1.9
3.00	2.98	-0.6	2.97	-1.0	3.03	+1.0

Under Conditions: $[\text{Fe}(\text{CN})_6]^{4-} = 7.5 \times 10^{-3} \text{ M}$, $[\text{phen}] = 4.50 \times 10^{-4} \text{ M}$, $\text{pH} = 3.0 \pm 0.02$, $I = 0.51 \text{ M}$ (KNO_3) and $\text{Temp.} = 25.0 \pm 0.1^\circ\text{C}$.

A spontaneous but not very significant change is recorded in the absorbance just after mixing the reagents for the reaction that can be observed by a slow change in absorption frequency. The very first change is given to fast reaction that occurs between 1,10 phenanthroline and $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{-3}$ which is present from before in the reaction medium due to photo and thermal decomposition of $[\text{Fe}(\text{CN})_6]^{4-}$. Thus, it is recommended to take solution that are freshly made, of $\text{K}_4[\text{Fe}(\text{CN})_6]$ before every kinetic run by proper dilutions from the stock solution in order to reduce the reaction that takes place in background. Expressions for catalyzed and un catalyzed reactions can be formed by utilising the well known Arrhenius equations to the rate constants and have been discussed below.

$$\frac{k_{\text{exp}}^c}{k_{\text{exp}}^u} = \frac{a_c e^{-E_a^c/RT}}{a_u e^{-E_a^u/RT}} \quad (6)$$

$$\frac{k_{\text{exp}}^c}{k_{\text{exp}}^u} = a' e^{(E_a^u - E_a^c)/RT} \quad (7)$$

In the above equation, the quotient of the pre-exponential factors are denoted as a_u and a_c for catalysed and uncatalysed reactions respectively and the corresponding activation energies are denoted as E_a^u and E_a^c ($E_a^u = 63.82 \pm 2.8 \text{ KJ Mol}^{-1}$ and $E_a^c = 61.25 \pm 2.6 \text{ KJ mol}^{-1}$). The ratio $K_{\text{exp}}^c / K_{\text{exp}}^u$ decreases only little with the increase in temperature. Therefore, a temperature of 25°C is taken as the most appropriate temperature. Consequently, the sensitivity of the reaction does not change to any appreciable extent a little increase in temperature. Therefore, we can select any suitable temperature for a complete set of kinetic runs but it is more easy to work at room temperature when the precision of thermostatic compartment is not present and the accuracy of the result is also not sacrificed to an appreciable extent.

From the expression given below, as per records of Tanaks's method [31] the detection limit was evaluated

$$\chi_{\text{D}} = \chi_{\text{B}} + t\sqrt{2\text{SB}}$$

χ_{D} denotes the statistical detection limit

χ_{B} denotes the average of blank value

$$\text{SB} = R/d_2,$$

here $R = \text{blank}_{\text{max}} - \text{blank}_{\text{min}}$.

To obtain SB from the range R of n replicates a factor $1/d_2$ is taken. It is sometimes advised to take $1/d_2 = 0.5908$ for the use of three blank calculations and take $t=3$ [31]. The detection limit calculated for the method using the specified conditions for the calibration equation at A_{15} corresponds to $2.5 \times 10^{-7} \text{ M}$ concentration of Pb^{+2} .

The very high sensitivity is obtained from the slope of the calibration curve at (A_{15}) and has the value of $3.3 \times 10^3 \text{ Lmol}^{-1}$. The sensitivity can be further enhanced by increasing the time interval to more

minutes like 20 or 25 minutes (Table 1) but this will result in the increase of the total time of analysis and will also increase the error %. Percentage errors in determining of lead at several concentrations in the range of 2.5×10^{-7} to 2.5×10^{-8} M are listed in Table 2.

To check the accuracy and precision of the above method for determining of lead, lead was also tested in presence of many ions at a fixed lead (II) concentration and results are tabulated in Table 3, the values of percentage errors are also given in the same table.

Table 3 is for determination of $[Pb^{+2}]$ in presence different interfering and non-interfering Cations and anions by using A_{15} Calibration Curves

Cyanide, Thiosulphate, and thiocyanate ions complex more easily with Pb^{+2} and thus reduce its catalytic activity. The interference caused due to Ni^{+2} , Cu^{+2} , Pb^{+2} , Cd^{+2} at very low lead concentration can be explained because of their ability to form salt with $[Fe(CN)_6]^{4-}$ [32].

TABLE 3. determination of $[Pb^{+2}]$ in presence different interfering and non-interfering Cations and anions by using A_{15} Calibration Curves

Ion	Ion Conc.taken $\times 10^7$ M	$[Hg^{+2}]$ found $\times 10^7$ M	%Error
Ni^{+2}	2.5	2.51	0.4
Pb^{+2}	2.5	2.50	0.0
Cd^{+2}	2.5	2.52	0.8
Cu^{+2}	2.5	2.49	0.4
EDTA	2.5	2.53	1.2
Oxalic Acid	2.5	2.50	0.0

Under Condition: $[Fe(CN)_6]^{4-} = 6.5 \times 10^{-3}$ M, $[phen] = 3.5 \times 10^{-4}$ M $[Pb^{+2}] = 3.0 \times 10^{-7}$ M, $pH = 3.0 \pm 0.02$, $I = 0.1$ M (KNO_3) and $temp = 25 \pm 0.1^\circ C$.

Applications of Determining Lead (II)

To check applicability, reliability, analytical capability and validity of method given by us some experiments to recover lead from various synthetic mixtures (SMs) containing other metals that usually occur with lead were carried out. Synthetic mixtures (SMs) were prepared because original samples containing traces of lead (II) along with other metals commonly found with lead were not available. The results have been tabulated in Table 4.

Table 4 is for Determination of lead (II) in various synthetic Mixtures and its application under the conditions specified before for A_{15} Curve.

TABLE 4. Determination of lead (II) in various synthetic Mixtures and its application under the conditions specified before for A_{15} Curve.

Synthetic Mixture (SM)	Composition of SM * Conc. $\times 10^7$ M	Pb^{+2} Found ** conc. $\times 10^7$ M	% Recovery
1	$Pb 0.30 + Cu 0.55$ $Co 1.75 + Cd 0.80$	0.32	101.2
2	$Pb 0.30 + Zn 2.25$ $Cd 0.80 + Ag 0.85$	0.29	99.0
3	$Pb 0.30 + Pb 0.87$ $Ni 0.40 + Cr 0.55$	0.33	101.7

Condition: * All of the metals are taken in +2 oxidation state
Except Ag^+ and Cr^{+3}

** Mean of at least three analysis were taken

4. CONCLUSION

Summarising the above chapter we can say that determination of lead in micro amounts in the range of 2.5×10^{-7} to 2.5×10^{-8} M in presence of various metal ions that are present in many folds i.e. 10-100 fold excess of lead can also be detected by this Kinetic method .

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