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A novel catalytic kinetic method for the determination of mercury(II) in water samples

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Mercury(II) ions act as catalyst in the substitution of cyanide ion in hexacyanoruthenate(II) by pyrazine (Pz) in an acidic medium. This property of Hg(II) has been utilized for its determination in aqueous solutions. The progress of reaction was followed spectrophotometrically by measuring the increase in absorbance of the yellow colour product, $[Ru(CN)_5Pz]^{3-}$ at 370 nm (λ_{max}, $\varepsilon = 4.2 \times 10^3$ M^{-1} s^{-1}) under the optimized reaction conditions; 5.0×10^{-5} M $[Ru(CN)_6^{4-}]$, 7.5×10^{-4} M [Pz], pH 4.00 ± 0.02, ionic strength (I) = 0.05 M (KCl) and temp. 45.0 ± 0.1 °C. The proposed method is based on the fixed time procedure under optimum reaction conditions. The linear regression (calibration) equations between the absorbance at fixed times (t = 15, 20 and 25 min) and [Hg(II)] were established in the range of 1.0 to 30.0 × 10^{-6} M. The detection limit was found to be 1.5×10^{-7} M of Hg(II). The effect of various foreign ions on the proposed method was also studied and discussed. The method was applied for the determination of Hg(II) in different wastewater samples. The present method is simple, rapid and sensitive for the determination of Hg(II) in trace amount in the environmental samples.

1. Introduction

Mercury (Hg) occurs naturally in the earth's crust.[1] Its concentration increases in the environment and water bodies due to the natural processes but mostly accelerated by the anthropogenic activities from pesticides, paints, batteries, industrial waste and land application of industrial or domestic sludge.[1,2] Thus, it gradually concentrates and moves away through the surface run-off transporting to the aquatic systems as rivers, lakes, seas and oceans.[2,3] Antagonistically to the organic contaminants, heavy metals such as Hg does not undergo microbial or chemical degradation and thus persist for a long time in the environment.[3,4] Therefore, heavy metals including Hg are the most hazardous pollutants to the environment because of the rapid industrialization and urbanization.[4] Thus, there has been continuous considerable emphasis on the Hg analysis in different type of samples.[5] Among the various heavy metals, particularly Hg has been listed as a priority pollutant by the international environmental and health agencies because of its persistence, bioaccumulation and toxicity (PBT) in the environment.[6] It not only causes serious health problems but also poses a great challenge to the environmental protection.[7,8]

Among other pollutants, Hg is of major concern in aquatic environments. Thus, Hg is considered as a global and recalcitrant pollutant due to its biogeochemical properties and its toxicity that can affect the health of human and ecosystems.[4]

Though metallic Hg is an insoluble element, it is easily oxidized to the soluble ionic form Hg^{2+} in the freshwater reservoirs and constitute a serious threat through the process of biomagnification.[9,10] Thus, mercury is of major concern in aquatic environments.[11] The consumption of contaminated fish, sea mammals and ground water are the prominent environmental sources of Hg exposure in humans.[11,12] It forms quite stable complexes with sulfhydryl (–SH) groups in the human body forming mercaptides having mobility through the tissues,[13] which lead to the inactivation of numerous enzyme reactions, amino acids and sulfur containing antioxidants such as *N*-acetyl cysteine (NAC), alpha-lipoic acid (ALA), and glutathione (GSH) and makes it quite toxic to the human being (*cf.* following general reaction).[14]

$$2R\text{–}SH + Hg^{2+} \rightarrow (R\text{–}S)_2Hg + 2H^+$$

The accumulation of Hg in the body is associated with hazardous health effects, such as gastrointestinal and nervous system disorders, respiratory and acute renal failures, hypertension, coronary heart disease (CHD), and cardiovascular disease (CVD).[15] Thus, even a small amount of Hg can have adverse effects on the human health.[16] One of the most stable forms of Hg is the highly toxic, water-soluble, divalent mercuric

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ion (Hg^{2+}), which is widely distributed in soil, air and aquatic environments as a result of illegal waste release from various anthropogenic and industrial activities. Hg^{2+} can cause serious environmental pollution and result in permanent damage to the biological organisms due to its acute and/or chronic toxicity.[17] Thus, the health and environmental issues associated with Hg^{2+} has stimulated researchers to develop inexpensive, effective and reliable methods for the detection and determination of Hg^{2+} sensitively and selectively.[5,7,8,17,18]

Attempts have been made to determine Hg in the environmental,[18] geological,[19] food[20,21] and biomedical[22,23] samples. Majority of the analytical methods proposed for the determination of Hg are based on the sophisticated techniques *viz.* cold vapor atomic absorption spectrometry (CV-AAS),[23–25] inductively coupled plasma mass spectrometry (ICP-MS),[26,27] atomic fluorescence spectrometry (AFS),[28,29] anodic stripping voltammetry (ASV),[30–32] high performance liquid chromatography (HPLC),[33,34] *etc.* All these techniques require expensive instrumentation, pre-concentration for the enrichment of analyte and its separation from the other constituents of the sample to minimize the matrix effect prior to their application. In addition, skilled operators, high cost, long time for running per sample, *etc.*, have been other disadvantages. To overcome these problems, attempts have been made to develop analytical methods based on the kinetics and catalysis,[5,18,35–38] formation of colored complexes of Hg(II) with other compounds,[39,40] *etc.* We have also been interested in developing analytical methods for the determination as well as removal of various analytes and toxic species of environmental, biological and medicinal interest.[5,18,35–38,41,42] Keeping the above explained backgrounds in mind, in the present communication, a successful attempt has been made to develop a novel, simple and precise catalytic kinetic method (CKM) for the trace level determination of Hg(II) in the aqueous samples which is based on the Hg(II) catalyzed substitution of (CN^-) in the $[Ru(CN)_6]^{4-}$ by pyrazine (Pz). The kinetics and mechanism of this reaction has already been reported by us[43] and has now been exploited as an indicator reaction system for the CKM in the determination of Hg(II). The developed CKM has successfully been utilized for the determination of Hg(II) in the wastewater samples.

2. Experimental

2.1 Reagents and instrumentation

All the reagents used were of analytical grade and deionized distilled water (DDW) was used throughout the study for preparation of all the solutions. The stock solutions (1.0×10^{-2} M) of $K_4[Ru(CN)_6]\cdot 3H_2O$, Pz and $HgCl_2$ were prepared by dissolving their appropriate amounts in DDW. $K_4[Ru(CN)_6]\cdot 3H_2O$ solution was kept in a dark amber colour volumetric flask to prevent its photodecomposition. The working solutions of these reagents were prepared by their appropriate dilution from the respective stock solutions as required. Potassium hydrogen phthalate (PHP)–HCl buffer of pH 4.00 ± 0.02 was prepared according to the literature reported method.[44]

Kinetic measurements and recording of various spectral scans were carried out in 10 mm matched quartz cuvettes using a Shimadzu UV-240 double beam spectrophotometer equipped with a self-designed thermostatic cell compartment. A remi ultra-cryostat was used to maintain the temperature of the reaction system. All the pH measurements were made on a Toshniwal digital pH meter model CL46. A certified 'A' grade volumetric apparatus were used throughout the work.

2.2 Procedure

All the required solutions were first placed in the thermostat maintained at 45.0 ± 0.1 °C for 30 min prior to their use to attain thermal equilibrium. 2.0 mL each of the solutions of Pz, buffer, $HgCl_2$ and $K_4[Ru(CN)_6]$ was pipetted out and mixed in a 10 mL volumetric flask, which was also placed in the same thermostat, shaken quickly and transferred immediately into a 10 mm spectrophotometric cuvette placed in the cell compartment of the spectrophotometer at 45.0 ± 0.1 °C. The progress of the reaction was monitored spectrophotometrically by measuring the increase in absorbance due to the formation of the product $[Ru(CN)_5Pz]^{3-}$ at its λ_{max} of 370 nm. A fixed time procedure was used to record the absorbance as a function of the concentration of Hg(II).The cuvettes were cleaned with acetone after few kinetic runs in order to remove the deposited intense yellow-colored $[Ru(CN)_5Pz]^{3-}$ complex.

3. Results & discussion

3.1 The indicator reaction

The detailed kinetics and mechanism of Hg(II) catalyzed substitution of CN^- in the $[Ru(CN)_6]^{4-}$ by Pz have been studied

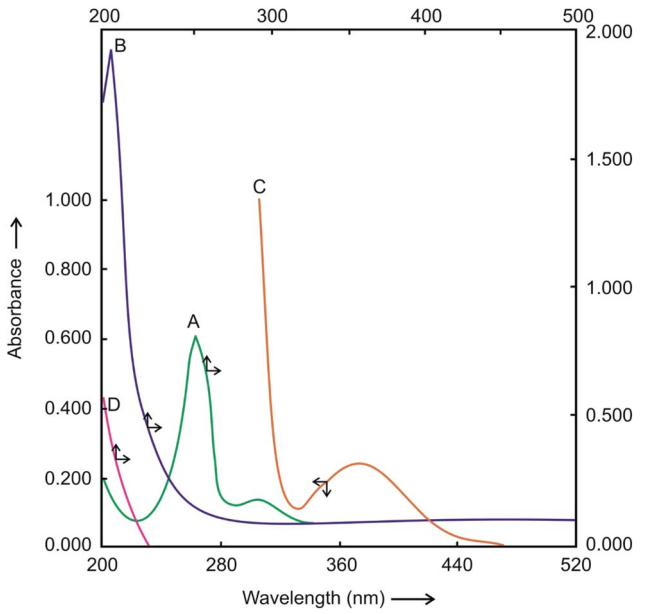

Fig. 1 UV-visible absorption spectra of reactants and products under the conditions: (A) [Pz] = 2.5×10^{-6} M, (B) $[Ru(CN)_6^{4-}] = 1.25 \times 10^{-5}$ M, (C) product $[Ru(CN)_5Pz^{3-}]$ formed by mixing $[Ru(CN)_6^{4-}] = 5.0 \times 10^{-5}$ M, [Pz] = 7.5×10^{-4} M, [Hg(II)] = 1.5×10^{-4} M, I = 0.05 M (KCl), pH = 4.00 ± 0.02 and temp. = 45.0 ± 0.1 °C, (D) [Hg(II)] = 1.0×10^{-4} M.

and reported by us earlier.[43] The reaction product, $[Ru(CN)_5Pz]^{3-}$ complex has strong absorption band at 370 nm and molar extinction coefficient $\varepsilon = 4.2 \times 10^3\ M^{-1}\ s^{-1}$. The UV-visible spectra of the reactants and the product shown in Fig. 1 clearly shows no interference between the absorbance of the product and reactants *i.e.* $[Ru(CN)_6]^{4-}$ and Pz. Hence, the progress of the reaction was easily followed spectrophotometrically by measuring the increase in absorbance at 370 nm *i.e.* λ_{max} of $[Ru(CN)_5Pz]^{3-}$ without making any corrections for the absorbance due to the reactants $[Ru(CN)_6]^{4-}$ and Pz.

3.2 The rate law and its analytical application

Based on the kinetic and mechanistic studies,[43] the overall rate of the indicator reaction comprises of the sum of the rate of the uncatalyzed as well as catalyzed reactions and is given by eqn (1).

$$\frac{d\left[Ru(CN)_5Pz^{3-}\right]}{dt} = k_1\left[Ru(CN)_6^{4-}\right] + \frac{k_2K\left[Ru(CN)_6^{4-}\right][Hg^{2+}][H_2O]}{1 + K\left[Ru(CN)_6^{4-}\right]} \quad (1)$$

If $K[Ru(CN)_6^{4-}] \gg 1$, eqn (1) reduces to eqn (2) as follows:

$$\frac{d\left[Ru(CN)_5Pz^{3-}\right]}{dt} = k_1\left[Ru(CN)_6^{4-}\right] + k_2'[Hg^{2+}] \quad (2)$$

In eqn (2), first term on the right hand side corresponds to the rate of the uncatalyzed path and k_2' involves the rate constant for the slow decomposition of the activated complex (formed between $[Ru(CN)_6]^{4-}$, Hg^{2+} and H_2O) and some other concentration terms.[43] Eqn (2) clearly shows a direct correlation between the rate of the indicator reaction and the concentration of Hg(II) and envisages for the accurate determination of Hg(II). In the present study, the rate of the uncatalyzed reaction is almost negligible. Thus, the catalytic kinetic method (CKM) for the determination of Hg(II) based on the $[Ru(CN)_6^{4-}]$–Pz indicator reaction will be more accurate in comparison to the other CKM involving the $[Fe(CN)_6^{4-}]$ – ligand indicator reactions.[35–38]

The increase in absorbance (A_t) at different time t (t = 15, 20 and 25 min) after mixing the reactants was recorded as a measure of the initial rate under the optimized reaction condition as 5.0×10^{-5} M $[Ru(CN)_5^{4-}]$, 7.5×10^{-4} M [Pz], pH 4.00 ± 0.02, ionic strength (I) 0.05 M (KCl) and temperature 45.0 ± 0.1 °C,[43] using fixed time procedure. The calibration curves were obtained by plotting the values of A_t against different Hg(II) concentrations where the corresponding linear regression equations correlating A_t to the [Hg(II)] obtained are shown in eqn (3)–(5).

$$A_{15} = 3.1 \times 10^3[Hg^{2+}] + 0.009 \quad (3)$$

$$A_{20} = 4.0 \times 10^3[Hg^{2+}] + 0.012 \quad (4)$$

$$A_{25} = 6.36 \times 10^3[Hg^{2+}] + 0.016 \quad (5)$$

3.3 Quantitative determination of Hg(II)

In order to validate the analytical applicability of the proposed CKM, recovery experiments were performed in various water samples spiked with Hg(II) and the results obtained for the three fixed times along with the standard deviations and the percentage errors are shown in Table 1. From Table 1, it is clear that the calibration curve corresponding to the A_{15} is a closer measure to the initial rate with the minimal percentage error as compared to A_{20} and A_{25}. Time less than 15 min and more than 25 min were not taken to minimize the experimental error. Based on this observation, the A_{15} calibration curve is recommended for the Hg(II) determination in the aqueous samples.

The detection limit (X_d), defined as three times standard deviation of the blank, was evaluated using Tanaka's method[45] using eqn (6), where X_b is the average of the blank values, $(SD)_b$ is the standard deviation of blank and equal to R/d_2, R is blank k_{max} − blank k_{min} and $1/d_2$ is a factor for obtaining $(SD)_b$ from the range R of n replicates whose value is recommended as 0.5908 for the use in three blank measurements.

Table 1 Evaluation of percentage error in the determination of Hg(II) under conditions: $[Ru(CN)_6^{4-}] = 5.0 \times 10^{-5}$ M, [Pz] = 7.5×10^{-4} M, pH = 4.00 ± 0.02, I = 0.05 M (KCl), temp. = 45.0 ± 1.0 °C

$[Hg^{2+}] \times 10^6$ M (taken)	A_{15}		A_{20}		A_{25}	
	$[Hg^{2+}] \times 10^6$ M (found)[b] ± SD[a]	Error (%)	$[Hg^{2+}] \times 10^6$ M (found)[b] ± SD[a]	Error (%)	$[Hg^{2+}] \times 10^6$ M (found)[b] ± SD[a]	Error (%)
1.00	0.94 ± 0.08	−6.00	0.94 ± 0.02	−6.00	1.06 ± 0.05	+6.00
2.00	2.25 ± 0.06	+12.50	2.00 ± 0.06	0.00	1.88 ± 0.03	+6.00
3.00	3.00 ± 0.08	0.00	3.05 ± 0.02	+1.67	3.06 ± 0.06	+2.00
4.00	4.02 ± 0.02	+0.50	4.05 ± 0.01	+0.80	4.06 ± 0.05	+1.50
5.00	5.05 ± 0.05	+1.00	5.05 ± 0.02	+1.00	5.03 ± 0.09	+6.00
10.00	10.00 ± 0.07	0.00	10.05 ± 0.06	+0.50	10.05 ± 0.06	+0.50
15.00	15.25 ± 0.02	+1.70	15.25 ± 0.03	+1.70	15.13 ± 0.04	+0.87
20.00	20.00 ± 0.03	0.00	20.02 ± 0.03	+0.10	20.25 ± 0.04	+1.25
30.00	29.80 ± 0.05	−0.67	29.50 ± 0.04	−1.70	30.25 ± 0.02	+0.83

[a] The ±SD values represent the % relative standard deviation of the mean for three determinations. [b] Mean of three determinations.

Table 2 Effect of different foreign ions on the determination of Hg(II) under the conditions: $[Ru(CN)_6^{4-}] = 5.0 \times 10^{-5}$ M, [Pz] = 7.5×10^{-4} M, $[Hg^{2+}] = 4.0 \times 10^{-6}$ M, pH = 4.00 ± 0.02, I = 0.05 M (KCl), temp. = 45.0 ± 1.0 °C

Foreign ion	[Foreign ion] (added), M	$[Hg^{2+}]$ (found), M	Error (%)	Inference
Mn^{2+}	2×10^{-4}	4.1×10^{-6}	+2.50	No inference
Ni^{2+}	4×10^{-4}	3.9×10^{-6}	−2.50	No inference
Ag^{+}	8×10^{-4}	4.0×10^{-6}	0.00	No inference
Sn^{2+}	8×10^{-4}	4.1×10^{-6}	+2.50	No inference
Pb^{2+}	4×10^{-4}	3.8×10^{-6}	−5.00	No inference
Mg^{2+}	4×10^{-4}	4.1×10^{-6}	+2.50	No inference
Ca^{2+}	4×10^{-4}	3.9×10^{-6}	−2.50	No inference
Cd^{2+}	4×10^{-4}	4.0×10^{-6}	0.00	No inference
Cu^{2+}	8×10^{-4}	3.8×10^{-6}	−5.00	No inference
Al^{3+}	4×10^{-4}	4.0×10^{-6}	0.00	No inference
Fe^{3+}	8×10^{-4}	3.9×10^{-6}	−2.50	No inference
Li^{+}	8×10^{-5}	1.2×10^{-6}	−70.00	Interfered
Co^{2+}	2×10^{-5}	1.6×10^{-6}	−60.00	Interfered
Zn^{2+}	4×10^{-5}	1.9×10^{-6}	−52.50	Interfered
Br^{-}	4×10^{-4}	4.1×10^{-6}	+2.50	No inference
I^{-}	8×10^{-4}	3.9×10^{-6}	−2.50	No inference
NO_3^{-}	8×10^{-4}	4.0×10^{-6}	0.00	No inference
CO_3^{2-}	8×10^{-4}	3.9×10^{-6}	−2.50	No inference
$C_2O_4^{2-}$	4×10^{-4}	4.0×10^{-6}	0.00	No inference
SO_4^{2-}	4×10^{-4}	4.1×10^{-6}	+2.50	No inference
NTA	2×10^{-4}	2.4×10^{-6}	−40.00	Interfered
IDA	2×10^{-4}	2.2×10^{-6}	−45.00	Interfered
EDTA	2×10^{-4}	1.9×10^{-6}	−52.50	Interfered

$$X_d = X_b + t\sqrt{2}(SD)_b \quad (6)$$

The detection limit for the present method corresponding to the A_{15} calibration curve under the optimized experimental conditions was found to be 1.5×10^{-7} M.

3.4 Interference study

The general precision and accuracy for the determination of Hg(II) by the proposed CKM was tested in the presence of several cations, anions and complexing agents. For this purpose, the recovery *i.e.* the determination of Hg(II) was performed using a fixed concentration of Hg(II), 4.0×10^{-6} M, in the presence of different known concentrations of individual cations, anions and complexing agents. The concentration of Hg(II) was determined using the A_{15} calibration eqn (3). The recovery results on the determination of 4.0×10^{-6} M Hg(II) in the presence of different individual cations, anions and complexing agents along with their concentrations have been presented in Table 2. Based on the results of Hg(II) recovered, it was confirmed that Mn^{2+}, Ni^{2+}, Ag^{+}, Sn^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Br^{-}, I^{-}, NO_3^{-}, CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-} ions did not interfere in the determination of Hg(II) but Li^{+}, Co^{2+}, Zn^{2+}, NTA, IDA, EDTA interfered significantly at their concentrations reported in Table 2. Metal hexacyanoferrates are very efficient sorbents for the recovery of alkali metal ions and especially Li^{+}, which leads to the formation of the corresponding lithium hexacyanoruthenate(II) complex as its Fe(II) counterpart in the solution.[46] Hence, a low recovery of Hg(II) is very much expected in the presence of Li^{+} ions in the aqueous medium. The interference by NTA, IDA, EDTA may be attributed to the possible ligand substitution between the monodentate cyanide ligand in $[Ru(CN)_6]^{4-}$ and the ligands *viz.* NTA, IDA, EDTA. Interference by Co^{2+}, Cu^{2+}, Zn^{2+} is probably due to the complex formation between these metal ions and $[Ru(CN)_6]^{4-}$ or Pz.

3.5 Validation and analytical application of CKM

In order to validate the proposed method, five water spiked synthetic mixtures (SMs) were prepared, which contained other metal ions along with the catalyst Hg(II). This was followed by the determination of Hg(II) in five different synthetic mixtures (SM-1 to SM-5) using the proposed CKM. The results were further confirmed by atomic absorption spectrophotometry (AAS), as shown in Table 3. The results obtained by CKM are in close agreement with those determined by AAS (Table 3).

After validation, the method was successfully applied for the determination of Hg(II) in the wastewater. For this, six wastewater samples (WWS-1 to WWS-6) were collected from our laboratory on different days and Hg(II) was determined using the proposed CKM. The results obtained for different WWS are

Table 3 Determination of Hg(II) in synthetic mixtures under optimized reaction conditions: $[Ru(CN)_6^{4-}] = 5.0 \times 10^{-5}$ M, [Pz] = 7.5×10^{-4} M, $[Hg^{2+}] = 4.0 \times 10^{-6}$ M, pH = 4.00 ± 0.02, I = 0.05 M (KCl), temp. = 45.0 ± 1.0 °C and its comparison atomic absorption spectrometry (AAS) method

Synthetic mixtures (SM)	Composition of SM (ng mL^{-1})	$[Hg^{2+}]$ found[b] ± SD[a] by CKM (ng mL^{-1})	Recovery (%)	$[Hg^{2+}]$ found[b] ± SD[a] by AAS (ng mL^{-1})
SM-1	Hg 1086.0 + Ca 4202.0 Cu 5006.0 + Cd 4808.0	1086.2 ± 1.1	100.02	1086.1 ± 4.3
SM-2	Hg 1086.0 + Ag 1206.5 Mg 4024.0 + Ni 1435.0	1085.9 ± 1.2	99.99	1085.9 ± 5.2
SM-3	Hg 1086.0 + Mn 3264.0 Ba 2244.0 + Cr 206.0	1086.6 ± 1.6	100.05	1086.1 ± 3.6
SM-4	Hg 1086.0 + Pd 2206.5 Al 1188.0 + Ag 608.0	1085.2 ± 1.8	99.93	1086.3 ± 3.6
SM-5	Hg 1086.0 + Ca 1224.0 Mg 1108.0 + Fe 906.0	1086.1 ± 1.1	100.01	1085.9 ± 5.5

[a] The ±SD values represent the % relative standard deviation of the mean for three determinations. [b] Mean of three determinations.

Table 4 Determination of Hg(II) in wastewater samples (WWS) under optimized reaction conditions: $[Ru(CN)_6^{4-}] = 5.0 \times 10^{-5}$ M, [Pz] = 7.5×10^{-4} M, pH = 4.00 ± 0.02, I = 0.05 M (KCl), temp. = 45.0 ± 1.0 °C and its comparison with the (AAS) method

Wastewater sample (WWS)	$[Hg^{2+}]$ found[b] ± SD[a] by CKM (ng mL^{-1})	$[Hg^{2+}]$ found[b] ± SD[a] by AAS (ng mL^{-1})	Error in CKM *versus* AAS (%)
WWS-1	224.06 ± 2.50	228.70 ± 3.26	+2.07
WWS-2	329.64 ± 4.35	331.65 ± 2.35	+1.44
WWS-3	244.16 ± 3.84	237.45 ± 4.50	−2.75
WWS-4	402.25 ± 4.36	408.24 ± 3.45	+1.50
WWS-5	398.17 ± 5.50	390.75 ± 3.60	−1.86
WWS-6	389.07 ± 5.50	407.08 ± 4.60	+4.63

[a] The ±SD values represent % relative standard deviation of the mean for three determinations. [b] Mean of three determinations.

shown in Table 4. The results obtained by CKM were also validated by AAS and were in excellent agreement with those determined by CKM (Table 3). The maximum error in the proposed CKM with respect to AAS is less than 5%, which is well accepted in the environmental analysis.

4. Conclusions

Though there are many sophisticated methods available for the Hg(II) determination but the present CKM based on the indicator reaction between $[Ru(CN)_6]^{4-}$–Pz offers a number of advantages over them, such as the unanalyzed reaction rate is negligible under specified reaction conditions and only 15 min is required for the Hg(II) determination without using any costly solvents and instruments. In addition, the method can be successfully applied for the determination of Hg(II) in the presence of a number of cations, anions and complexing agents with very good sensitivity. In conclusion, the proposed CKM is quite sensitive, quick, economical and superior to few known methods including CKM.[35–38] It can selectively be applied for the Hg(II) determination at micro-level in environmental water samples.

Conflicts of interest

The authors are declare that there is not any conflict of interest including any financial, personal or other relationships with other people or organizations.

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