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Flow injection fluorimetric determination of chromium(VI) in electroplating baths by luminescence quenching of tris(2,2′-bipyridyl) ruthenium(II)

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Abstract

A sensitive and selective luminescence quenching method is developed and used for manual and flow injection analysis (FIA) of chromium(VI) by reaction with $[Ru(bpy)_3]^{2+}$. The emission peak of ruthenium(II) at 595 nm is linearly decreased as a function of Cr(VI) concentration. This permits determination of chromium(VI) ion over the concentration range 0.1–20 $\mu g\,ml^{-1}$ with a detection limit of 33 $ng\,ml^{-1}$. The quenching process is due to an electron transfer from the luminescent $[Ru(bpy)_3]^{2+}$ complex ion to Cr(VI) resulting in the formation of the non-luminescent $[Ru(bpy)_3]^{3+}$ complex ion. Selectivity for Cr(VI) over many anions and transition, alkali and alkaline earth metal cations is demonstrated. High concentration levels of sulphate, chloride, borate, acetate, phosphate, nitrate, cyanide, Pb^{2+}, Zn^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Mn^{2+} ions are tolerated. The effects of solution pH and $[Ru(bpy)_3]^{2+}$ reagent concentration are examined and the reaction conditions are optimized. Validation of the method according to the quality assurance standards show suitability of the proposed method for use in the quality control assessment of Cr(VI) in complex matrices without prior treatment. The method is successfully applied to determine chromium(VI) in electroplating baths using flow injection analysis. Results with a mean standard deviation of ±0.6% are obtained which compare fairly well with data obtained using atomic absorption spectrometry.

Keywords: Luminescence quenching; Ruthenium tris bipyridyl; Determination of chromium(VI); Flow injection analysis; Electroplating chromium waste

1. Introduction

Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. These compounds are frequently added to cool water for corrosion control [1], used in the manufacture of ink pigments, generated largely by metal cleaning processes, surface finishing and metal coating [2]. Therefore, accurate determination of chromium is important for monitoring environmental pollution and for quality control of industrial products. Effluents from industrial facilities dealing with chromium are frequently monitored to ensure proper chromium removal prior to release into the environment.

Methods available for measuring chromium in water samples include spectrophotometry [3–10], electrometry [11–13], titrimetry [14], colorimetry [15], atomic absorption spectrometry [16,17] and ion chromatography [18,19]. Some of these methods suffer from interference by many common ions, and require prior time consuming separation step. Direct fluorimetric methods have been reported for the determination of Cr(VI) in water [20–22]. These methods are not sensitive enough for measuring less than 2 $\mu g\,ml^{-1}$, suffer from severe interferences by Fe(II), Pb(II) and Hg(II) and used over very narrow range of concentrations.

Fluorescence quenching methods for the determination of Cr(VI) based on the reaction with 2,6,7-tris hydroxy-9-(3,5-dibromo-4-hydroxyphenyl) fluorine-emulgent OP [23], rhodamine 6G [24], rhodamine-B [25], tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) [26], disodium-1-(4-

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Table 1
General characteristics of some fluorimetric methods for the determination of Cr(VI)

Reagent	$\lambda_{ex}/\lambda_{em}$	Linear range ($\mu g\, ml^{-1}$)	Detection limit ($\mu g\, ml^{-1}$)	Major interference	Reaction time (min)	Reference
2,4,7-Tris hydroxy-9-(3,5-dibromo-4-hydroxypheny) fluorine-emulgent OP	365/582	0.002–0.006	0.002	NR	20	[23]
Rhodamine 6G	525/545	0.08–0.8	0.08	Ce^{4+}, NO_2^-, Cu^{2+}, Fe^{3+}, Pb^{2+}	5	[24]
Rhodamine-B/H_2O_2	348/548	0.01–0.16	0.033	Cu^{2+}, Cr^{3+}, Fe^{3+}, I^-	NR	[25]
Tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II)	450/610	5–60	1.22	Ce^{4+}, NO_3^-, CN^-	NR	[26]
		0.1–5	0.433			
Disodium-1-(4-hydroxy-salicylideneamino)-8-hydroxynaphthalene-3,6-di sulphonate	361/420	0.5–2	0.075	VO_3^{2-}, MoO_4^{2-}	10	[27]
2,3,7-Trihydroxy-9-dibromo hydroxyphenylfluorone (DBH-PF)	470/520	0.002–0.02	0.002	NR	NR	[28]
L-Tyrosine	285/308	0.27–5.5	0.27	Ag^+, Co^{2+}, Pb^{2+}, Fe^{3+}, Ce^{4+}	NR	[29]
Dibromophenylfluorone	432/505	0.002–0.2	NR	MnO_4^-, Fe^{3+}	NR	[30]
N-(2-Pyridyl)quinoline-2-carbothioamide (PTQA)	360/500	NR	NR	$S_2O_3^{2-}$, $S_2O_8^{2-}$, Ag^+, Cu^{2+}, Hg^{2+}, Ce^{4+}	NR	[31]
Poly-4-vinylaniline nanoparticles	306/380	0.1–13	0.02	Sr^{2+}, Fe^{2+}	>1	[32]
1-Pyrenemethylamine nanoparticles	238/400	0.36–32	0.15	Mn^{7+}, Hg^{2+}, Co^{2+}	10	[33]
o-Vanilline-8-amino quinoline	280/314	8.2–130	2.5	Co^{2+}, Pb^{2+}, Hg^{2+}, Be^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, As^{3+}, Al^{3+}	10	[34]
8-Hydroxy quinoline 5-sulfinic acid	360/450	0.29–0.78	NR	Pb^{2+}, Hg^{2+}, Ce^{4+}, V^{5+}, Sc^{4+}, NO_3^-, BrO_3^-	15	[35]
Safranine-T/H_2O_2	516/586	0–0.12	0.026	Cu^{2+}, Bi^{3+}, Cr^{3+}, Fe^{3+}	20	[36]
Tris(2,2′-bipyridyl) ruthenium(II)	453/595	0.01–20 0.01–2	0.02 0.01	Ce^{4+}	<1	This work

NR: not reported.

hydroxylsalicylideneamino)-8-hydroxynaphthalene-3,6-disulfonate [27], 2,3,7-trihydroxy-9-dibromohydroxy-phenylfluorone (DBH-PF) with hexadecyltrimethyl ammonium bromide [28], L-tyrosine [29], dibromophenylfluorone [30], 2-(α-pyridyl) thioquinaldinamide [*N*-(2-pyridyl) quinoline-2-carbothioamide] [31], poly-4-vinylaniline nanoparticles [32], 1-pyrenemethylamine nanoparticles [33], vanilline-8-aminoquinone [34], 8-hydroxyquinoline-5-sulfonic acid [35] and safranine-T [36] have been described. Advantages and limitations of these methods are presented in Table 1.

Luminescence quenching of tris(2,2′-bipyridyl) ruthenium(II), $[Ru(bpy)_3]^{2+}$, by various inorganic and organic substrates has been investigated and proved to proceed by electron or energy transfer mechanism [37]. This reagent, however, has not been utilized for quantification purposes. Since, the oxidative quenching of $[Ru(bpy)_3]^{2+}$ complex ion ($E^{\mathrm{ox}}_{3+/2+}$ is 1.26 V [38]), and the redox potential of the system Cr(VI)/Cr(III) ($E_{6+/3+}$ is 1.33 V [39]) electron transfer reaction between the two species are expected, this offers a promising approach for fluorimetric determination of Cr(VI).

The present work evaluates the use of dynamic quenching of $[Ru(bpy)_3]^{2+}$ for Cr(VI) measurements. In the presence of ambient oxygen, fluorescence quenching of $[Ru(bpy)_3]^{2+}$ is detected in the presence of Cr(VI) and used for quantification of submicrogram levels of Cr(VI). The method offers the advantages of high sensitivity, good selectivity and ease of operation in addition to the commercial availability of the fluorophore reagent and its high stability. The method is used to determine a wide range of chromium concentration in industrial wastewater under static and dynamic mode of operations. Flow injection analysis of 0.1–2.0 $\mu g\, ml^{-1}$ Cr(VI) displays results with a mean standard deviation of 0.6%.

2. Experimental

2.1. Apparatus

All luminescence measurements were made with an LS-50B luminescence spectrometer (Perkin-Elmer) equipped with a 20 kW xenon discharge lamp for excitation for 8 μs duration. $[Ru(bpy)_3]^{2+}$ luminescence was measured by setting the excitation monochromator to 453 nm with a 1.0 nm slit width and the emission monochromator to 595 nm with a 7.5 nm slit width. All pH adjustments were made with an Orion (model 720) pH/mV meter and a HORIBA pH combined electrode (model F-22E). The flow injection analysis

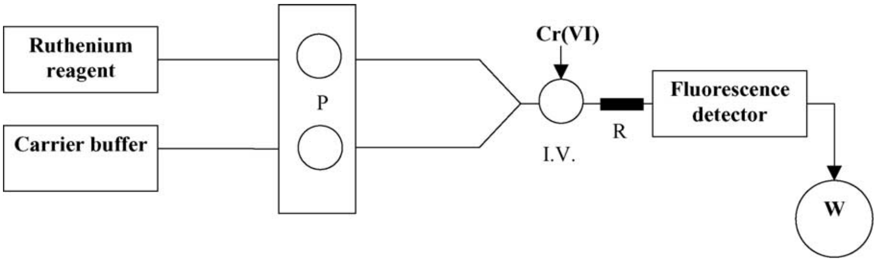

Fig. 1. Flow injection manifold for fluorimetric determination of Cr(VI); I.V., injection valve; P, peristaltic pump; R, reaction coil; W, waste.

(FIA) system consisted of a Manostat cassette pump (Junior, NY) and an Omnifit injection valve (Omnifit, Cambridge, UK) with sample loop of 100 μl volume. The flow Tygon tubes were obtained from (ALKEM) (P/N A00349 and P/N A000355), the pump tubes were red/red 0.71 in. i.d. and blue/blue 0.065 in. i.d. The distance between the injection valve and the detector was 30 cm and a reaction coil (length 50 cm) was used. Atomic absorption spectrometric measurements of Cr(VI) were made at 357.9 nm with Perkin-Elmer AAS spectrometer (model 3100) using the recommended optimum conditions [40].

2.2. Reagents

All chemicals were of analytical reagent grade. Deionized, distilled water was used throughout. Phosphoric acid 85%, acetic acid (glacial) and boric acid were obtained from Fluka. Chromium standard 10^{-2} mol l^{-1} stock solution was made by dissolving dried 0.2941 g $K_2Cr_2O_7$ in 100 ml deionized water. $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ was purchased from Aldrich and used as received. Aqueous solution of tris(2,2′-bipyridyl) ruthenium(II) hexahydrate chloride was freshly prepared. Universal buffer solutions were prepared by mixing 0.04 mol l^{-1} phosphoric, acetic and boric acids as reported [39] followed by pH adjustment with 0.2 mol l^{-1} NaOH.

2.3. Calibration curve and analytical procedure

Aliquots of $Cr_2O_7{}^{2-}$ stock solutions containing (0.1–20 μg ml^{-1}) were transferred to 10-ml volumetric flasks followed by 1.00 ml of 100 μmol l^{-1} $[Ru(bpy)_3]^{2+}$ reagent. The solutions were completed to the mark with a universal buffer of pH 4. The luminescence intensity at 595 nm was measured after 1 min. The decrease in the luminescence of the reagent as a function of Cr(VI) concentration was measured.

The flow injection manifold was constructed according to the schematic diagram presented in Fig. 1. A perstaltic pump was used to pump equal volumes of $[Ru(bpy)_3]^{2+}$ reagent and the carrier buffer (pH 4) through the system. The sample was injected through an injector loop (100 μl) to a mixing tee where it was mixed at room tempreature with the $[Ru(bpy)_3]^{2+}$ reagent. These two solutions were allowed to mix and equilibrate for 1 min before proceeding to the fluorometer detector. The decrease in the luminescence intensity of the reagent as a function of Cr(VI) concentration was measured according to Stern–Volmer relationship ($I_0/I = 1 + K_{sv}[Q]$) where I_0 and I are the luminescence intensities in the absence and presence of Cr(VI), K_{sv} Stern–Volmer constant and $[Q]$ denotes the concentration of Cr(VI). In the FIA measurements, I_0 and I were taken as the mean intensities of at least three signals just before and after sample injection and appearance of the signal.

2.4. Determination of Cr(VI) in industrial wastewater samples

Wastewater samples collected from different electroplating facilities were filtered through Whatman filter paper no. 41 before analysis. A 1.00 ml aliquote of the filtrate was mixed with 10 ml of 1 mol l^{-1} H_2SO_4, diluted to 1l with deionized water, and shaken well. A 1.00 ml aliquot of the test solution was transferred to 10-ml volumetric flask followed by 1.0 ml of 100 μmol l^{-1} $[Ru(bpy)_3]^{2+}$ solution. The mixture was completed to the mark with universal buffer of pH 4. A blank experiment was made under identical conditions. The luminescence intensity was measured and Cr(VI) concentration was determined as described above.

3. Results and discussion

3.1. Nature of the reaction between Cr(VI) and $[Ru(bpy)_3]^{2+}$

The luminescence of $[Ru(bpy)_3]^{2+}$ was found to decrease with the addition of Cr(VI) as a result of the electron transfer from $[Ru(bpy)_3]^{2+}$ to Cr(VI) and formation of the non-luminescent $[Ru(bpy)_3]^{3+}$ complex ion. As shown in Fig. 2, the excitation and emission spectra of the $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$–Cr(VI) systems are similar (intensity at the same wavelength). The excitation and emission wavelengths are 453 and 595 nm, respectively. The luminescence intensity of $[Ru(bpy)_3]^{2+}$ decreased upon addition of Cr(VI) without any spectral shift.

3.2. Effect of pH

In an attempt to identify the optimum pH for the measurement, the effect of pH on the excitation and emission

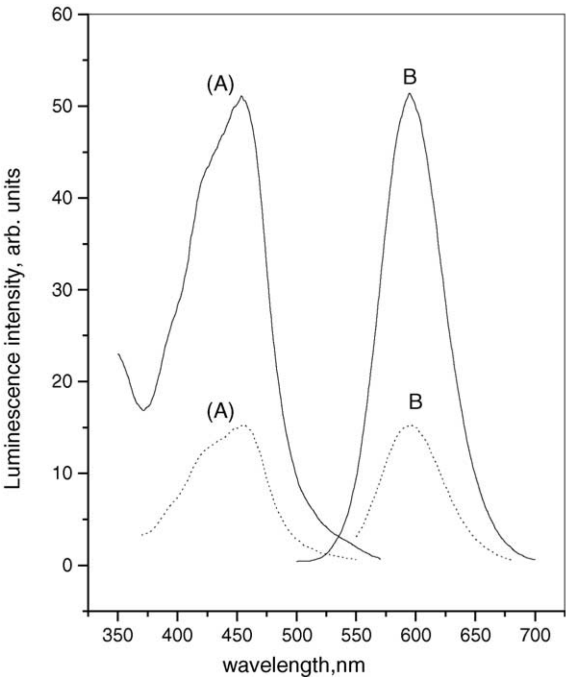

Fig. 2. Excitation (A) and emission (B) spectra of $[Ru(bpy)_3]^{2+}$ in the absence (—) and presence (- - -) of 5 μg ml^{-1} Cr(VI).

spectra of ruthenium complex reagent was examined. It was found that the luminescence quantum yield of $[Ru(bpy)_3]^{2+}$ reagent was not affected by the changes in pH. The pH effect on the quenching process showed that the ratio of I_0/I was high upto pH 6 and declined suddenly beyond this pH value (Fig. 3). It has been reported that Cr(VI) exists at pH 2–6 in the form of $Cr_2O_7{}^{2-}$ and $HCrO_4{}^{-}$ with E_o of +1.232 and +1.35 V, respectively [37,41]. In pH > 6, however, $CrO_4{}^{2-}$ is predominantly present with E_o −0.13 V. This confirms the significant progress of the reaction only in acidic media.

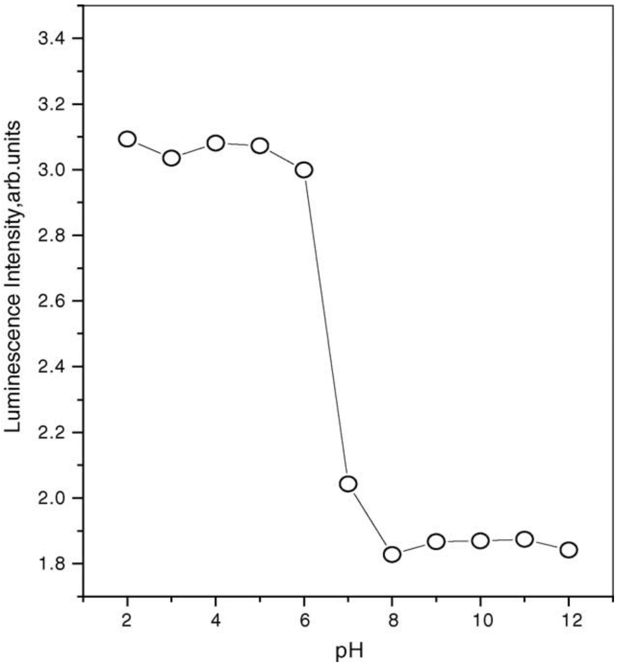

Fig. 3. Effect of pH on the luminescence intensity of $[Ru(bpy)_3]^{2+}$ reagent (10 μmol l^{-1}) in the presence of 2 μg ml^{-1} of Cr(VI).

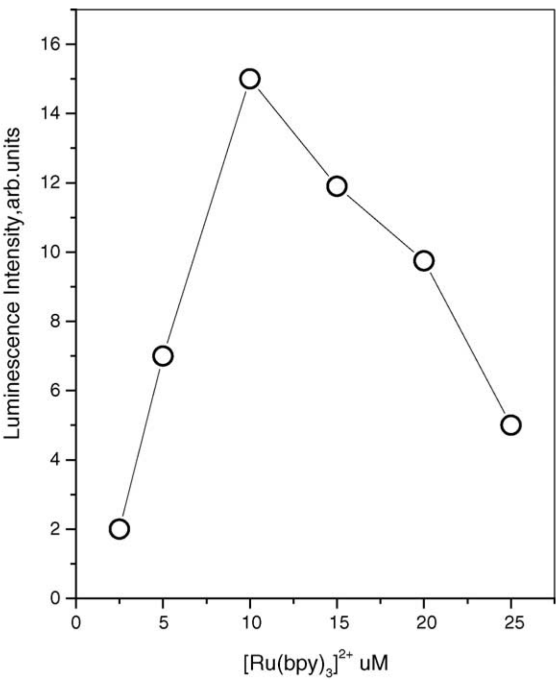

Fig. 4. Effect of $[Ru(bpy)_3]^{2+}$ concentrations on the response of 2 μg ml^{-1} of Cr(VI) at pH 4.

3.3. *Effect of fluorophore concentration*

The effect of $[Ru(bpy)_3]^{2+}$ complex ion concentration on the extent of luminescence quenching of 2 μg ml^{-1} Cr(VI) was tested using different concentrations of $[Ru(bpy)_3]^{2+}$ reagent ranging from 1 to 25 μmol l^{-1}. Luminescence quenching measurements revealed that 10 μmol l^{-1} of $[Ru(bpy)_3]^{2+}$ complex ion was the optimum concentration (Fig. 4); higher concentrations caused self quenching leading to decrease the sensitivity.

3.4. *Calibration curve of Cr(VI)*

Fig. 5 shows the calibration curve of Cr(VI) under static mode of operation using 10 μmol l^{-1} of $[Ru(bpy)_3]^{2+}$ reagent at pH 4. The luminescence measured at 595 nm with an excitation at 453 nm of $[Ru(bpy)_3]^{2+}$ decreased upon using various Cr(VI) concentrations. The luminescence intensity was decreased linearly with increasing Cr(VI) concentration over the range 0.1–20 μg ml^{-1}. The linear regression equation is: $F_0/F = 0.1865C$ (ppm) + 0.0025 with a correlation coefficient of 0.9995 ($n = 10$). The lower limit of detection (LOD) calculated according to IUPAC recommendations [42]: LOD = KS_o/S where S_o is the standard deviation of the blank measurements ($n = 6$), S is the slope of the calibration curve and K is a numerical factor depending on the degree

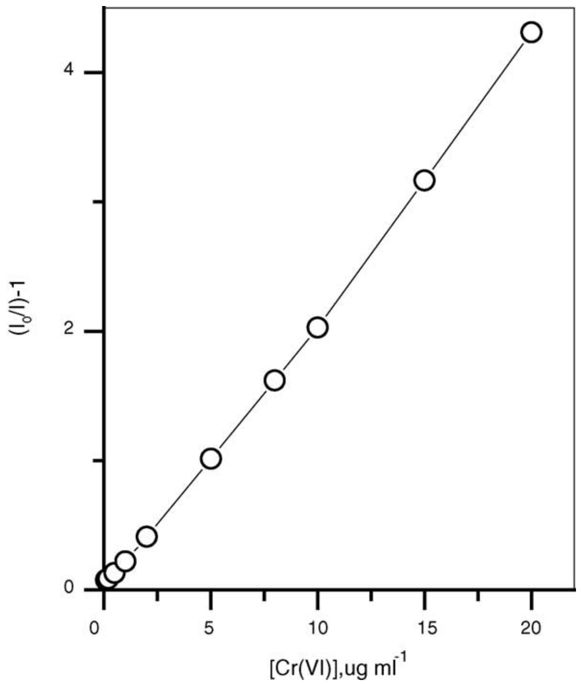

Fig. 5. Stern–Volmer plot for the quenching of $[Ru(bpy)_3]^{2+}$ reagent complex by various concentrations of Cr(VI).

of confidence level needed. With $K = 3$ (i.e. $3S_o$), the limit of detection of the proposed method was 33 ng ml^{-1}. The assay method for Cr(VI) ions over the concentration range 0.5–10 μg ml^{-1} was validated according to the quality assurance standards [43]. Six batches (six determinations each) were used for measuring accuracy, precision, range, lower limit of detection, repeatability (Cv_w) and between-day variability (Cv_b). The results obtained are presented in Table 2. A statistical F-test analysis of the results indicated that at the 95% confidence level, the method showed no statistical difference.

3.5. Flow injection analysis

The Stern–Volmer plot was examined with data collected for measuring Cr(VI) using FIA system operated at pH 4, flow rate 2.7 ml min^{-1} and $[Ru(bpy)_3]^{2+}$ reagent concentration of 100 μmol l^{-1}. Validation of the method under hydrodynamic mode of operation was carried out using successive injections of 0.1–2 μg ml^{-1} Cr(VI) and statistical treatment of the data as described [43]. The linear response covered the range 0.1–2 μg ml^{-1}, the standard deviation was ±0.41% and the lower limit of detection was 18 ng ml^{-1} with 100 μl sample size. The resulting calibration plot is presented in Fig. 6. Linear regression analysis indicated a slope of 0.13 ± 0.01 μg ml^{-1}, an r^2 of 0.9993 over the tested chromium concentration range (0.1–2.0 μg ml^{-1}) and an output rate of 25 samples per hour.

Table 2
Response characteristics (validation) of the fluorimetric assay methods used for manual and FIA of Cr(VI)

Parameter	Static (manual)	Hydrodynamic (FIA)
Linear range (μg ml^{-1})	0.1–20	0.1–2
Detection limit (ng ml^{-1})	33	18
Working rang (pH)	2–5	2–5
Standard deviation (σ_v) (%)	0.3	0.4
Accuracy (%)	100.4	99.8
Repeatability (Cv_w) (%)	0.3	0.4
Between-day variability (Cv_b) (%)	0.6	0.5
Sample size (ml)	>1.0	<0.1
Output per hour (sample)	<10	>25

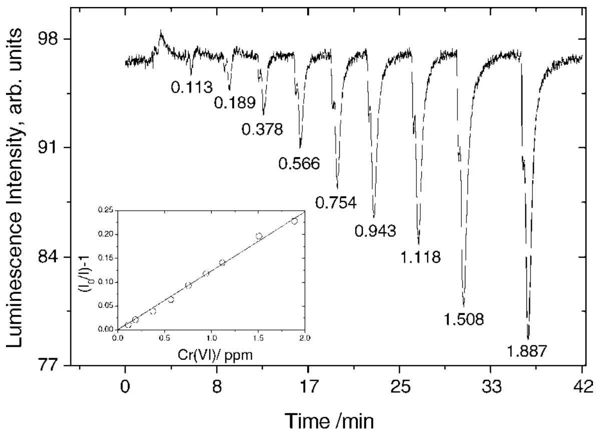

Fig. 6. Luminescence intensity time trace and Stern–Volmer plot for different concentrations of Cr(VI) by FIA at pH 4.

3.6. Interferences

Under the optimized conditions, the effect of 30 foreign ions on the luminescence intensity of $[Ru(bpy)_3]^{2+}$ in the presence of 1 μg ml^{-1} of Cr(VI) was examined. Effects of cations and anions were made with salt solutions containing their nitrate and sodium counter ions, respectively. It has been reported that the coexisting alkali metal cations affect the quenching reaction rate of $[Ru(pby)_3]^{2+}$ complex with Cr^{3+} without any significant effect on the emission spectrum of the complex [44]. The tolerance limits of foreign ions were taken as the maximum amounts causing a change of ±5% in the luminescence intensity (Table 3). It can be seen that most of cations and anions examined did not interfere, even when present in as high as >300-fold excess over Cr(VI). Cyanide ion did not interfere at levels up to 150-fold excess over Cr(VI). In the present work, Pb^{2+}, Cu^{2+}, NO_3^{-} and $S_2O_3^{2-}$ ions which caused serious interference with the previously published methods [24,25,31,34–36] were tolerated when present at ∼1000-fold excess over Cr(VI). However, Ce^{4+}ions seriously interfere.

3.7. Analytical applications

Cr(VI) contents of the wastewater of some electroplating baths were selectively determined using the proposed fluorescence FIA system based on ruthenium luminescence quench-

Table 3
Effect of foreign ions on the quenching of tris(2,2′-bipyridyl) ruthenium(II)

Foreign ion	Tolerance ratio (w/w)	Error (%)
K^+	1000	−3.52
Co^{2+}	400	−2.26
Pb^{2+}	450	−2.01
Al^{3+}	400	−3.50
Ba^{2+}	400	−2.26
Mn^{2+}	310	+1.50
Ni^{2+}	300	+1.00
Cd^{2+}	550	+4.02
Ca^{2+}	550	−4.02
Cu^{2+}	700	−0.75
Hg^{2+}	540	−2.51
Zn^{2+}	200	+2.76
Mg^{2+}	300	+1.76
Li^+	1000	−4.27
Ce^{4+}	0.5	−2.50
Fe^{3+}	187	−2.50
$SeO_3{}^{2-}$	800	−1.51
Cl^-	2100	−2.41
Br^-	1000	−3.51
I^-	70	−4.20
$SO_4{}^{2-}$	1000	−4.10
$NO_3{}^-$	900	−2.31
$NO_2{}^-$	30	−4.80
CN^-	150	−3.41
SCN^-	1000	−2.81
$ClO_4{}^-$	2000	−1.75
EDTA	2200	−4.65
$S_2O_3{}^{2-}$	450	−2.50
$SO_3{}^{2-}$	750	−1.50
$CO_3{}^{2-}$	900	+1.60

Table 4
Flow injection fluorimetric determination of chromium(VI) in exhausted electroplating baths

Sample	Cr(VI) ($\mu g\ ml^{-1}$)		Difference (%)
	AAS	Fluorimetry	
1	6.65 ± 0.21	6.64 ± 0.40	0.15
2	2.49 ± 1.20	2.50 ± 0.61	0.40
3	4.48 ± 0.52	4.38 ± 0.90	2.23

Average of six measurements.

ing. The results obtained (Table 4) compared favorably with data obtained by atomic absorption spectrometry. This revealed that no interference was posed by the complex sample matrix.

4. Conclusions

A fast and simple fluorimetric method is used for determination of Cr(VI) under static (manual) and hydrodynamic (FIA) mode of operations by reaction with $[Ru(bpy)_3]^{2+}$reagent. Quenching of luminescence of the reagent is linearly related to Cr(VI) concentration over the range 0.1–20 $\mu g\ ml^{-1}$ (manual) and 0.01–2 $\mu g\ ml^{-1}$ (FIA). The method is sufficiently selective to monitor Cr(VI) concentration in the presence of many interfering ions commonly present in the effluent of metal finishing electroplating processes. A comparison with some other previously suggested fluorimetric methods (Table 1) reveals that the present assay method covers a wider concentration range [24,25,27–29,35,36], displays lower detection limit [24–27,29,31,34], requires no prior treatment step and exhibits higher selectivity in the presence of Cu^{2+}, Pb^{2+}, CN^-, $NO_3{}^-$ and $S_2O_3{}^{2-}$ ions [24–29,31,34–36].

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