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Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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A novel fluorescent distinguished probe for Cr (VI) in aqueous solution

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ARTICLE INFO

Article history: Received 15 December 2008 Received in revised form 6 June 2009 Accepted 7 June 2009

Keywords: Chromium (VI) Salicylaldehyde rhodamine B Spectrofluorimetric Oxidation reaction

ABSTRACT

Salicylaldehyde rhodamine B hydrazone (SRBH) was developed as a new spectrofluorimetric probe for the selective and sensitive detection of $\text{CrO}_4{}^{2-}$ in acidic conditions. The proposed method was based on the special oxidation reaction between non-fluorescent SRBH by potassium dichromate to produce a highly fluorescent rhodamine B, as a product. Under the optimum conditions described, the fluorescence enhancement at 591 nm was good linearly related to the concentration of $\text{CrO}_4{}^{2-}$ from 1.0×10^{-8} to 3.0×10^{-7} M (0.42–12.6 ng mL⁻¹) with a correlation coefficient of R^2 = 0.9989 (n = 10) and a detection limit of 1.5×10^{-9} M (0.063 ng mL⁻¹). The relative standard deviation (R.S.D.) was 2.0% (n = 6). The proposed method was also successfully applied to the determination of chromium (VI) in drinking water, river water and synthetic samples.

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1. Introduction

Chromium (Cr) exists in different oxidation states in the groundwater, seawater, and soil of our environment [1]. Trivalent Cr is an essential trace element in the human body as a part of the glucose tolerance factor and also plays an important role in lipid and protein metabolism. However, hexavalent Cr form is well known to be high toxic and carcinogenic. Chromium (VI) enters natural waters mainly through effluents from the electroplating and tanning industries, from sanitary landfill leaching, and from water-cooling towers. It can also enter the drinking water distribution system from the corrosion inhibitors used in the water pipes [2]. So, the concentration of Cr (VI) in drinking water is strictly regulated to a lower micromolar level by the governments of many nations [3]. To monitor the quality of drinking water and the risks of industrial wastes, many methods with high sensitivity is explored to ensure the availability of Cr (VI) determination at low but harmful concentration levels. Furthermore, good selectivity is also necessary to tolerate the interference of some commonly coexistent foreign ions, such as Na (I), K (I), Ca (II), Cd (II), Ni (II), Cu (II), Zn (II), Hg (II), Cl⁻, SO₄²⁻, NO₃⁻, relatively non-toxic Cr (III) [4] and another pollutant As (V) [5,6]. But Cr (VI) was found in two forms such as $Cr_2O_7^{2-}$ and CrO_4^{2-} in the water matrix. As our well known, CrO₄²⁻ is stable in neu-

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tral and alkaline environments, while $Cr_2O_7^{2-}$ in acidic conditions. Alternately, the CrO_4^{2-} can convert into $Cr_2O_7^{2-}$ under acidic environment, and vice versa. In the past 20 years, concern about the presence of hexavalent Cr in the environment resulted in the development of numerous analytical techniques for the determination of Cr (VI) in different sample matrices. Besides the flow injection analysis [7,8], on-line selective determination of both species is by chromatography [9–11], mass spectrometry [12,13] or atomic absorption spectrometry [14–17]. Solvent extraction [18,19] and ion exchange [20,21] are still one of the most extensively used methods for separation and preconcentration of Cr (VI). They tend to be complicated and expensive to apply even though endowing with high selectivity and sensitivity. Recent, two types of microcantilever sensors for highly sensitive detection of CrO_4^{2-} have been reported [22,23]. Among them, the spectrofluorimetry methods utilizing Cr (VI)-selective fluorescent probes are of particular interests because of its rapid, simple, highly sensitive and selective advantages. However, many reported fluorescent probes for Cr (VI) generally undergo a fluorescence quenching upon the oxidation by Cr (VI), which is generally not as sensitive as a fluorescence enhancement response. A series of fluorescent nanoparticles (NPs) were synthesized and applied in selective detection of Cr (VI) ions in water samples [24–28]. Up to date, a fluorescence enhancement method for detection of Cr (VI) has been proposed based on the oxidation of non-fluorescent rhodamine B hydrazide by Cr (VI) in acidic aqueous solutions [29].

In this paper, salicylaldehyde rhodamine B hydrazine (SRBH) as a novel fluorescent probe was facilely synthesized and explored to indicate Cr (VI) in aqueous solution. Based on a special oxida-

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Scheme 1. Procedures for the synthesis of SRBH.

tion effect of Cr (VI) on the non-fluorescent SRBH to produce highly fluorescent rhodamine B in acidic conditions as a product, a new highly sensitive fluorescent and colorimetric method for Cr (VI) was proposed. The advantages of this method over other reported fluorescent procedures are: long emission wavelength (>550 nm) avoiding the influence of background fluorescence (<400 nm); even higher sensitivity due to the significant fluorescence enhancement signals; and facile analysis at room temperature without heating and preconcentration. Furthermore, a significant pink color occurred in the presence of Cr (VI), which could be developed a new "naked-eye" method for indication of Cr (VI) in aqueous solutions. In addition, SRBH could be served as an effective probe for illumination of the stoichiometric ratio as 1:2 of Cr₂O₇^{2–} and CrO₄^{2–} based on their different response to probe.

2. Experimental

2.1. Apparatus and reagents

The absorption spectra were acquired on a Hitachi U-3010 spectrophotometer (Tokvo, Japan). All fluorescence measurements were made with a Hitachi F-4500 Fluorescence Spectrophotometer (Tokyo, Japan) equipped with a plotter unit and a 1 cm quartz cell. NMR spectra were recorded using a JOEL INMECA300 spectrometer operated at 300 MHz. All pH measurements were made with a Model pHs-3c meter (Shanghai, China). Deionized water (distilled) was used throughout the experiment as the solvent. All the reagents were purchased from commercial suppliers (Beijing Chemical Reagent Co., China; Acros; Fluka) and used without further purification. The solutions of Cr (VI), As(V), $S_2O_8^{2-}$, MnO₄⁻, NO₂⁻, ClO₃⁻, BrO₃⁻, IO₃⁻ and H₂O₂ were prepared from K₂CrO₄, NaAsO₃, K₂S₂O₈, NaNO₂, KMnO₄, KClO₃, KBrO₃, KlO₃ and 30% H₂O₂, respectively. The solutions of other metal ions were prepared from their nitrate or chloride salts. Stock solutions of chromium (VI), H₂SO₄, and rhodamine B hydrazide were prepared as follows: first, Cr (VI) stock solution $(1.00 \times 10^{-3} \text{ M})$: in a 100 mL standard flask, Cr (VI) stock solution $(1.00 \times 10^{-3} \text{ M})$: in a 100 mL standard flask, 14.7 mg potassium dichromate (K₂Cr₂O₇) and 19.4 mg potassium chromate (K₂CrO₄) was dissolved in 5 mL water, and then diluted to the mark respectively. Second, H₂SO₄ stock solution (0.20 M): in a 10 mL standard flask. 1.60 mL sulfuric acid solution was dissolved in 5 mL water, and then diluted to the mark. Finally, salicylaldehvde rhodamine B hvdrazide stock solution in DMF (1.00×10^{-3} M): in a 10 mL standard flask, 5.45 mg salicylaldehyde rhodamine B hydrazide was dissolved in 5 mL DMF, and then diluted to the mark with DMF.

2.2. Synthesis of salicylaldehyde rhodamine B hydrazide (SRBH)

The SRBH as a fluorescent probe for Cr (VI) was synthesized through two steps according to literatures [30,31]. First, rhodamine hydrazide (RBH) was synthesized by a modified procedure according to Yang's [32] and Tong's methods [29]. After drying under an

IR light, a high product yield of RBH as a pink solid was obtained for use of followings. Rhodamine hydrazide (1, 0.46 g, 1.0 mmol) was dissolved in 20 mL absolute ethanol. An excessive salicylaldehyde (4.0 mmol) was added then the mixture was refluxed in an air bath for 6 h. After that, the solution was cooled (concentrated to 10 mL) and allowed to stand at room temperature overnight. The precipitate that appeared next day was filtered and washed 3 times with 10 mL cold ethanol. After being dried under reduced pressure, and the reaction afforded 0.30 g, 2 (55%) as a white solid (as shown in Scheme 1).

Compound 2. ESI mass spectrometry: m/z 545.3 (95% [M+H]⁺), 567.1 (5% [M+Na]⁺); M⁺ calculated 544.3. ¹H-NMR (CDCl₃), δ (ppm): 1.15 (t, 12H, NCH₂CH₃, J=7.1 Hz), 3.31 (q, 8H, NCH₂CH₃, J=7.1 Hz), 6.24 (dd, 2H, Xanthene-H, J_1 =8.8 Hz, J_2 =2.3 Hz), 6.43 (d, 2H, Xanthene-H, J=2.3 Hz), 6.52 (dd, 2H, Xanthene-H, J_1 =8.8 Hz, J_2 =2.3 Hz), 7.11 (d, 1H, Ar-H), 7.26 (m, 3H, Ben-H), 7.48 (m, 2H, Ben-H), 7.54 (m, 2H, Ar-H), 7.98 (d, 1H, Ar-H), 8.65 (bs, 1H, N=C-H). 13C-NMR (DMSO-d6) δ (ppm): 12.9, 44.1, 66.0, 97.8, 106.0, 108.5, 123.5, 124.4, 127.3 (2C, 127.3, 127.4), 128.1, 129.4 (2C, 129.3, 129.4 respectively), 130.8, 134.4, 135.1, 148.4, 149.0, 151.6, 153.3 and 164.3.

2.3. Analytical procedure

The fluorescence "turn-on" reaction of SRBH with Cr (VI) was conducted in 10 mM H₂SO₄ buffer. Typically, to a reaction solution containing 10 mM H₂SO₄ buffer and 1×10^{-7} M SRBH, an appropriate volume of sample solution with a final Cr (VI) concentration of not more than 1×10^{-7} M was added, and the final volume was adjusted to 10 mL with deionized water. After 15 min, a 3 mL portion of the solution was transferred to a 1-cm quartz cell, and the fluorescence intensity/spectrum was measured at room temperature with $\lambda_{ex}/\lambda_{em} = 520/591$ nm and both excitation and emission slit widths of 5 nm. In the meantime, a blank solution containing no Cr (VI) was prepared and measured under the same conditions for comparison. Because of the determination of Cr (VI) at low concentrations, Cr (VI) stock solutions of 1.0×10^{-4} and 1.0×10^{-5} M were prepared by diluting the original stock solution, and proper amount of these solutions was used in the analytical procedure.

3. Results and discussion

3.1. Spectral characteristics of salicylaldehyde rhodamine B hydrazone (SRBH)

It has been reported that the rhodamine derivative SRBH is a colorless and non-fluorescent substance due to its stable "spirolactam form" [33]. In this work, it was also observed that the fluorescence of 10^{-5} M SRBH even in 10 mM H₂SO₄ aqueous medium was very weak and only about 1/300 of that of 10^{-5} M rhodamine B (RB) under the same condition. This suggested the possibility of fluorogenic determination of substances, which could successfully convert SRBH to RB under this acidic condition. Recently, salicylaldehyde fluorescein



Fig. 1. Fluorescence excitation (left) and emission (right) spectra of SRBH in the absence and presence of Cr (VI): (from bottom to top ($\times 10^{-7}$ M): 0.0, 0.1, 0.2, 0.3, 0.5, 0.75, 1.0 1.5, 2.0 and 3.0 Cr (VI). Conditions: 1.0×10^{-7} M SRBH, 10 mM H₂SO₄ and 15 min reaction time at room temperature.

hydrazone were applied in a colorimetric logic chemosensor for pH and Cu (II) [31]. Furthermore, salicylaldehyde rhodamine B hydrazone displayed a selective and sensitive for sensing of Cu (II) based on metal-ligand complex and opening-spirolactam ring effect [30]. With careful investigations, a significant enhancement of fluorescence and continuous red shift of emission peak from 573 to 585 nm was observed upon the addition of Cu (II) compared to that of only SRBH under the same conditions. The optical changes including fluorescence enhancement and wavelength red shift were attributed to the opening ring and the increase of molecule's conjugation due to Cu (II)-binding to SRBH, respectively. In addition, the utilization of the conversion of RBH to RB had already been carried out to detect Cu (II) [33] and peroxynitrite [32] in neutral aqueous media. In this work, interestingly, it was found that in highly acidic conditions, the addition of Cr (VI) to SRBH aqueous solution could cause a significant enhancement of fluorescence, which was similar to that of RB molecule. The fluorescence spectra of SRBH in the absence and presence of different amounts of Cr (VI) are shown in Fig. 1. It can be found that SRBH displays no obvious spectral characteristics in either its excitation or emission spectra. However, a significant restore of fluorescence with an excitation maximum at 564 nm and an emission maximum at 591 nm was observed when Cr (VI) was added.

A gradual blue-shift of fluorescence spectra of SRBH were found in the presence of Cr (VI) compared to original SRBH solution resulting from the oxidation of SRBH to RB by Cr (VI) in the acidic conditions. A significant enhancement of fluorescence intensity of solution was attributed to opening-spirolactam ring, as a product of RB. These results were similar to Tong groups' findings. The



Fig. 2. Effect of sulfuric acid concentration on the fluorescence intensity. Conditions: 1.0×10^{-7} M SRBH, 1.0×10^{-7} M Cr (VI) and 15 min reaction time at room temperature. Excitation/emission was performed at $\lambda_{ex}/\lambda_{em}$ = 520/591 nm.

schematic of interaction between SRBH and Cr (VI) was shown in Scheme 2. In addition, a more direct evidence was obtained by comparing the pure RB solution fluorescence spectra to SRBH-Cr (VI) under the same environments (these results are not shown). The characteristics exaction around 358, 413, 522 and 564 nm, and emission centered 591 nm of SRBH-Cr (VI) system were completely same as the pure RB solution.

3.2. Optimization of the analytical procedures

3.2.1. Effect of H_2SO_4 concentration

As our well known, 0.1 mol L⁻¹ of H₂SO₄ was generally chosen to control the acidity of system. The effect of H₂SO₄ concentration on the fluorescence intensity at 591 nm for 1.0×10^{-7} M Cr (VI) and SRBH was illustrated in Fig. 2. No fluorescence enhancement could be observed when the reaction system was lack of H₂SO₄, suggesting the important role of acidic condition in the oxidation reaction of Cr (VI) and SRBH. The fluorescence intensity at 591 nm increased with the concentration of H₂SO₄ first, and then slightly decreased. The maximum and stable fluorescence enhancement occurred in the range of 7.5–30 mM H₂SO₄. High concentration of H₂SO₄ could cause a significant enhancement of the blank fluorescence of RBH in water due to the formation of open ring form. Therefore, a concentration of 10 mM H₂SO₄ was then chosen.

3.2.2. Effect of SRBH concentration

Effect of SRBH concentration on the sensitivity of the proposed method for detection of Cr (VI) was investigated. The results shown in Fig. 3 indicated that a maximum fluorescence enhancement was observed when $0.05-2.0 \,\mu$ M SRBH reacted with $0.1 \,\mu$ M Cr (VI) in





Fig. 3. Effect of RBH concentration on the fluorescence intensity Conditions: 10 mM H_2SO_4 , 0.1 μ M Cr (VI) and 15 min reaction time at room temperature. Excitation/emission was performed at $\lambda_{ex}/\lambda_{em}$ = 520/591 nm.

10 mM H_2SO_4 for 15 min. Excess SRBH was found to give only mild interference to the fluorescence blank signal. In this work, 0.10 μ M SRBH was chosen. This concentration of SRBH was also applied to the determination of Cr (VI) at the lower micromolar level to ensure the acceptable reaction rate with desirable analysis characteristics.

3.2.3. Effect of reaction time

The kinetic characteristics of the reaction system of SRBH and Cr (VI) were first investigated and shown in Fig. 4. Upon the addition of 0.5 and 1.0 μ M Cr (VI) to the SRBH (1.0×10^{-7} M) solution in the presence of 10 mM H₂SO₄, a stable fluorescent signal at 591 nm could be obtained within a reaction time of 10 min and remained constant for at least 1 h. It was also found that higher concentration of the reagents was of benefit to the rate of the reaction. An incubation time of 15 min was chosen for this work as a practical matter. An accurate and reproducible result could be obtained at this relatively short reaction time.

3.3. Interference of foreign ions

As shown in Table 1, the interference of some foreign ion species to 0.1 μ M Cr (VI) under the optimum condition was examined. To maintain the relative error within 5.0%, most of the ions could be allowed at high concentrations (>100-fold) of that of Cr (VI)). Fe (III) and S₂O₈²⁻ had mild interference and should be kept at no



Fig. 4. Kinetic behavior of the fluorescence of the SRBH–Cr (VI)–H₂SO₄ reaction system. Squares: 1.0×10^{-7} M SRBH only; dots: 1.0×10^{-7} M SRBH and $0.5 \,\mu$ M Cr (VI); triangles: 1.0×10^{-7} M SRBH and $1.0 \,\mu$ M Cr (VI); conditions: $10 \,\text{mM} \,\text{H}_2$ SO₄ and 15 min reaction time at room temperature. Excitation/emission was performed at 520/591 nm.

Table 1

Tolerance of foreign ions in the determination of 1.0×10^{-7} M Cr (VI).

Ions added	Tolerance ratio (mol/mol)
$ \begin{array}{l} Na^{+}(Cl^{-}),K^{+}(Cl^{-}),Ca^{2+}(NO_{3}^{-}),Mg^{2+}(NO_{3}^{-}),\\ Ba^{2+}(NO_{3}^{-}),Al^{3+}(Cl^{-}),Mn^{2+}(NO_{3}^{-}),Co^{2+}(NO_{3}^{-}),\\ Ni^{2+}(SO_{4}^{2-}),Cu^{2+}(SO_{4}^{2-}),Zn^{2+}(NO_{3}^{-}),Pb^{2+}(NO_{3}^{-}),\\ Hg^{2+}(NO_{3}^{-}),Cd^{2+}(NO_{3}^{-}),Cr^{3+}(NO_{3}^{-}),(Na^{+})SO_{4}^{2-},\\ (K^{+})CO_{3}^{2-},(K^{+})NO_{3}^{-} \end{array} $	>500
$Fe^{2+}(Cl^{-}), Fe^{3+}(SO_4^{2-}), (K^+)S_2O_8^{2-}$	20
H_2O_2	10
(K ⁺)ClO ₃ ⁻ , (K ⁺)BrO ₃ ⁻ , (K ⁺)IO ₃ ⁻	5
(K ⁺)MnO ₄ ⁻ , (Na ⁺)NO ₂ ⁻	0.5

Conditions: 10 mM H₂SO₄, 1.0×10^{-7} M SRBH and 15 min reaction time at room temperature. Excitation/emission was performed at 520/591 nm.

more than 10-fold of that of Cr (VI), while H_2O_2 might be oxidized by Cr (VI) and its concentration should be lower than 5-fold. The major interferences come from these strong oxidants such as CIO_3^- , BrO_3^- , IO_3^- , MnO_4^- and NO_2^- which might oxidize SRBH or bleach RB. However, the proposed method is still of good selectivity.

3.4. Cr (VI) ion analysis properties of SRBH probe

According to the above procedure, the calibration curve for the determination of Cr (VI) was constructed under the opti-



Fig. 5. (A) Photographs of $1.0 \,\mu$ M SRBH as a selective 'naked-eye' probe for Cr (VI) in 10 mM H₂SO₄ medium, the concentration of Cr (VI) from left to right are (×10⁻⁶ M): 0.00, 0.05, 0.10, 0.30, 0.50, 1.00 and 5.00; (B) UV-vis absorption spectra of SRBH in 10 mM H₂SO₄. Concentrations of Cr (VI) are (×10⁻⁶ M): 0.00, 0.01, 0.03, 0.05, 0.10, 0.30, 0.50, 1.50 and 3.00.

Table 2

Comparison the analytical performances of familiar method for detection Cr (VI) ion.

Reagents	Regression equation (10 ⁻⁶ M)	Linear range (10 ⁻⁶ M)	LOD (10 ⁻⁶ M)	Method
Microcantilever sensor	-	0.001-1000	0.001	[23]
AN/PAM NPs	$F_0/F = 0.94667 + 2.1606C (\mu g m L^{-1})$	0.769–39.5	0.384	[24]
MagneticFe ₃ O ₄ /Py/PAM nanocomposites	$F_0/F = 0.9573 + 3.6572C (g m L^{-1})$	1.92-269.8	0.384	[27]
Poly-4-vinylaninline NPs	$F_0/F = 1.055 + 0.067C (\mu g m L^{-1})$	1.92-250.6	0.384	[28]
Rhodamine B hydrazide	-	0.05-2.00	0.0055	[29]
Salicylaldehyde rhodamine B hydrazone	$\Delta_{\rm IF}$ = -11.97 + 2429C CrO ₄ ²⁻	0.01-0.30	0.0015	This work

mum condition, which was: $10 \text{ mM} \text{ H}_2\text{SO}_4$, $1.00 \times 10^{-7} \text{ M}$ SRBH, 15 min reaction time, excitation/emission at 520/591 nm at room temperature. The linear range was at least $0.10-3.00 \times 10^{-7}$ M $(0.42-12.6 \text{ ng mL}^{-1})$ with a correlation coefficient of $R^2 = 0.9989$ (n=10). The detection limit, based on the definition by IUPAC $(LOD = 3S_{b} m^{-1})$, was found to be $1.5 \times 10^{-9} M (0.063 \text{ ng mL}^{-1})$ from 10 blank solutions. The relative standard deviation (R.S.D.) for six repeated measurements of 4.2 ng mL^{-1} Cr (VI) was 2.0%. When SRBH was incubated with various amounts of Cr (VI) ion, a dramatic color change from colorless to purple was observed (Fig. 5A) and the characteristic absorption of initial RB molecule at about 585 nm gradually returned (Fig. 5B). Under the acidic condition of 10 mM H_2SO_4 , there was a linear relationship between the absorbance at 585 nm and the concentration of Cr (VI). These results suggested that SRBH could severe a simple "naked-eye" probe for accurate indication of Cr (VI) ion in the water samples.

In view of the linear range and detection limit of methods, some familiar methods for Cr (VI) ions with organic fluorescent dyes and functionalized organic and inorganic nanoparticles are summarized in Table 2. Evaluation from analytical performances, we can find very clearly that our proposed method exhibited lower detection blank and detection limit than most of current used and recently described fluorescent methods for detection of Cr (VI) ion (see the results in Table 2).

3.5. Exploration to indication of Cr (VI) ion formations in the water

To our well known, Cr (VI) ion was found two anionic forms such as $Cr_2O_7^{2-}$ and CrO_4^{2-} in the water matrix. The CrO_4^{2-} form could be stable in neutral and alkaline environments, while $Cr_2O_7^{2-}$ in acidic condition. Furthermore, the form of CrO_4^{2-} can convert into $Cr_2O_7^{2-}$ under acidic environment, and vice versa. The pH-dependent dimerization equilibrium for chromate dianion could be expressed as followings equation:

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$
(1)

In the 10 mM H₂SO₄ medium, the fluorescence "turn-on" of SRBH occurred in the presence of Cr (VI) as $Cr_2O_7^{2-}$ specie. As illustrated in Eq. (1), the stoichiometric ratio of $Cr_2O_7^{2-}$ and CrO_4^{2-} was 1:2, which displayed one molecule of $Cr_2O_7^{2-}$ corresponding to two molecules of CrO_4^{2-} . Under the same conditions, the two plots of the fluorescence intensity of SRBH via the concentration of $Cr_2O_7^{2-}$ and CrO_4^{2-} were shown in Fig. 6.

Table 3			
Determination	of Cr (VI) in	the synthetic	samples.



Fig. 6. Two plots of fluorescence intensity of SRBH via the concentrations of $Cr_2O_7^{2-}$ and CrO_4^{2-} . Black squares represented $Cr_2O_7^{2-}$ anions and red triangles represented CrO_4^{2-} anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

According to above-proposed procedure, the calibration curves for the determination of Cr (VI) for $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} anions were constructed under the optimal conditions. The linear range for $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} all is 0.01–0.3 μ M and the linear regression equation is as follows: $\Delta_{\rm IF} = -11.97 + 2429$ C CrO_4^{2-} (μ M), with a correlation coefficient of 0.9989 (n = 10) and $\Delta_{\rm IF} = -29.12 + 5044$ C CrO_7^{2-} (μ M), with a correlation coefficient of 0.9993 (n = 10), respectively. We can cleanly find that the slope of the linear regression equation for $\text{Cr}_2\text{O}_7^{2-}$ anions is approximately double than its' for CrO_4^{2-} . The result is consistent with the stoichiometric ratio between $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} as 1:2. These results suggested that SRBH could serve an effective fluorescent probe for indication of Cr (VI) formations: $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} in water solution.

3.6. Applications of the method in real samples determination of Cr (VI)

Under optimal experimental conditions, the present method was applied to determine Cr (VI) in synthetic samples and wastewaters. Table 3 shows, the results obtained for the synthetic samples. The results show that the present method can be applied to direct determination of Cr (VI) without separation of Cr (III). Samples of

Cr (VI) in samples (10 ⁻⁷ M)	Cr (III) in samples (10 ⁻⁷ M)	Cr(VI) found (10 ⁻⁷ M)	Recovery ^a (%)	R.S.D. (%)
0.5	0.5	0.504	101	1.8
1.0	2.0	1.02	102	1.9
1.5	3.0	1.52	101	2.0
2.0	5.0	2.06	103	2.5

Conditions: 10 mM H_2SO_4 , 1.0×10^{-7} M SRBH and 15 min reaction time at room temperature. Excitation/emission was performed at 520/591 nm. ^a Average of six determinations.

Determination of Cr (VI) in real water samples.

Water sample	Found value (mea	$n \pm \sigma$, $n = 5$) (10 ⁻⁷ M)	Added standard solution (10 ⁻⁷ M)	Found total value (10 ⁻⁷ M)	Recovery (%)
	DPCI method ^a	The presented method ^a			
Drinking-water	-	-	1.00	1.05 ± 0.02	105
River-water	2.50 ± 0.05	2.60 ± 0.04	1.00	3.65 ± 0.02	102
Waste-water sample 1	50.0 ± 0.1	51.0 ± 0.2	10.0	60.8 ± 0.3	99.6
Waste-water sample 2	75.0 ± 0.2	75.5 ± 0.3	10.0	86.5 ± 0.2	101

^a Average of six determinations.

wastewater were collected from an industrial effluent collection point in an industrial zone consisting of chemicals, tanning, and dyes industries. The waste-water samples were filtered and condensed 100-folds with rotary evaporation. The water was boiled with HNO₃ to remove some coexisting organic substances and neutralized with NaOH before determination. Results obtained from two individual determinations are shown in Table 4. Recovery of the method was checked by analyzing the waste-water samples by the DPCI standard method [34] recommended for the determination of Cr (VI) in waters. Recovery values obtained are in the range 99.2–101.5%, which demonstrated the applicability of the method is free from interferences when applied to the analysis of wastewater.

4. Conclusions

A "turn-on" fluorescent method for detection of Cr (VI) was developed based on the special oxidation reaction between non-fluorescent SRBH by potassium dichromate to produce a highly fluorescent rhodamine B, as a product. The proposed method has a linear range of $0.10-3.00 \times 10^{-7}$ M (0.42-12.6 ng mL⁻¹) Cr (VI) with a detection limit of 1.5×10^{-9} M (0.063 ng mL⁻¹). Furthermore, this method endowed with using of simple instrumentation and methodology. Meantime, the synthetic SRBH molecules could severe a simple "naked-eye" probe for selective detection of Cr (VI) ion, and explored to indicate Cr (VI) ions from $Cr_2O_7^{2-}$ and CrO_4^{2-} anions. Furthermore, it was successfully applied to the monitoring of Cr (VI) in environmental samples in agreement with the standard method.

Acknowledgments

The authors acknowledge the support from the Education Commission Natural Science Foundation of Anhui Province (No. 2006kj153B, 2006jql204, 2008jp1101).

References

- [1] R.M. Cespon-Romero, M.C. Yebra-Biurrun, M.P. Bermejo-Barrera, Preconcentration and speciation of chromium by the determination of total chromium and chromium (III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system, Anal. Chim. Acta 327 (1996) 37–45.
- [2] M. Boussemart, C.M.G. Vandenberg, Preconcentration of chromium (III) from sea-water by adsorption on silica and voltammetric determination, Analyst 119 (1994) 1349–1353.
- [3] For the list of drinking water contaminants in China, see: http://www.envir. gov.cn/law/standard/6.htm; for that in USA, see: http://www.epa.gov/ safewater/mcl.htmL#mcls, 2005 (in Chinese).
- [4] S.L. Brauer, K.E. Wetterhahn, Chromium (VI) forms a thiolate complex with glutathione, J. Am. Chem. Soc. 113 (1991) 3001–3007.
- [5] M. Sittig, Priority Toxic Pollutants, Health Impacts and Allowable Limits, Noyes Data Corporation, 1980, p. 158.
- [6] C.N. Sawyer, R.L. McArty, Chemistry for Environmental Engineering, McGraw Hill, New York, 1978.
- [7] T.M.A. Razek, S. Spear, S.S.M. Hassan, Selective measurement of chromium (VI) by fluorescence quenching of ruthenium, Talanta 48 (1999) 269–275.
- [8] P. Singer, A. Melissa, J.H. Aldstadt III, A comparative study of diffusion samplers for the determination of hexavalent chromium by sequential injection spectrophotometry, Microchem. J. 74 (2003) 47–57.

- [9] P. Pretici, F. Borgherini, G. Vitulli, High pressure liquid chromatography resolution of racemic mixtures of chiral tricarbonyl arene chromium (0) and cyclopentadienyl-titanium (IV) complexes, Inorg. Chim. Acta 268 (1998) 323–327.
- [10] R. Ganeshjeevan, R. Chandrasekar, S. Yuvaraj, G. Radhakrishnan, Determination of hexavalent chromium by on-line dialysis ion chromatography in a matrix of strong colourants and trivalent chromium, J. Chromatogr. A 988 (2003) 151–159.
- [11] I. Ali, H.Y. Aboul-Enein, Speciation of arsenic and chromium metal ions by reversed phase high performance liquid chromatography, Chemosphere 48 (2002) 275–278.
- [12] E. Skrzydlewska, M. Bdlcerzak, F. Vanhaecke, Determination of chromium, cadmium and lead in food-packaging materials by axial inductively coupled plasma time-of-flight mass spectrometry, Anal. Chim. Acta 479 (2003) 191–202.
- [13] Y.R. Li, N.K. Pradhan, R. Foley, G.K.C. Low, Selective determination of airborne hexavalent chromium using inductively coupled plasma mass spectrometry, Talanta 57 (2002) 1143–1153.
- [14] M.I.C. Monteiro, I.C.S. Fraga, A.V. Yallouz, N.M.M. de Oliveira, S.H. Ribeiro, Determination of total chromium traces in tannery effluents by electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometric methods, Talanta 58 (2002) 629–633.
- [15] X.S. Zhu, B. Hu, Z.C. Jiang, M.F. Li, Cloud point extraction for speciation of chromium in water samples by electrothermal atomic absorption spectrometry, Water Res. 39 (2005) 589.
- [16] Y.Z. He, M. Garrido-Ecija, M. de la Cuardia, On-line bidirectional electrostacking of chromium (III) and chromium (VI) for flame atomic absorption spectrometry determination, Anal. Chim. Acta 421 (2000) 57–65.
- [17] K. Ohta, H. Uegomori, S. Itoh, T. Mizuno, Microchem. J. 56 (1997) 343.
- [18] B.A. Zeev (Ed.), Determination of Trace Element, VCH, Weinheim, 1994, p. 121.
- [19] G.J. de Jong, U.A. Brinkman Th, Determination of chromium(III) and chromium(VI) in sea water by atomic absorption spectrometry, Anal. Chim. Acta 98 (1978) 243–250.
- [20] S.L. Lo, S.F. Shiue, Recovery of Cr (VI) by quaternary ammonium compounds, Water Res. 32 (1998) 174–178.
- [21] S. Katsuta, N.J. Suzuki, Radioanal, Nucl. Chem. 222 (1997) 45-50.
- [22] Y.F. Zhang, H.F. Ji, G.M. Brown, T. Thundat, Detection of CrO₄²⁻ using a hydrogel swelling microcantilever sensor, Anal. Chem. 75 (2003) 4773–4777.
- [23] H.F. Ji, T.G. Thundat, R. Dbestani, G.M. Brown, P.F. Britt, P.V. Bonnesen, Ultrasensitive detection of CrO₄²⁻ using a microcantilever sensor, Anal. Chem. 73 (2001) 1572–1576.
- [24] L. Wang, T.T. Xia, J.S. Liu, L.Y. Wang, H.Q. Chen, L. Dong, G.R. Bian, Preparation and application of a novel core/shell organic nanoparticle as a fluorescence probe in the selective determination of Cr (VI), Spectrochim. Acta A 62 (2005) 565–569.
- [25] L. Wang, G.R. Bian, L. Dong, T.T. Xia, S. Hong, H.Q. Chen, Preparation of fluorescent polyvinyl alcohol keto-derivatives nanoparticles and selective determination of chromium (VI), Spectrochim. Acta A 65 (2006) 123–126.
- [26] L.Y. Wang, L. Wang, T.T. Xia, L. Dong, H.Q. Chen, L. Li, Selective fluorescence determination of chromium (VI) with poly-4-vinylaninline nanoparticles, Spectrochim. Acta A 60 (2004) 2465–2468.
- [27] S. Hong, H.Q. Chen, Leyu Wang, Lun Wang, Luminescent and magnetic Fe₃O₄/Py/PAM nanocomposites for the chromium(VI) determination, Spectrochim. Acta A 70 (2008) 449–453.
- [28] S.K. She, Y.Y. Zhou, L. Zhang, L.Y. Wang, L. Wang, Preparation of fluorescent polyvinyl alcohol keto-derivatives nanoparticles and selective determination of chromium (VI), Spectrochim. Acta A 62 (2005) 711–715.
- [29] Y. Xiang, L. Mei, N. Li, A.J. Tong, Sensitive and selective spectrofluorimetric determination of chromium (VI) in water by fluorescence enhancement, Anal. Chim. Acta 581 (2007) 132–136.
- [30] Y. Xiang, A. Tong, P. Jin, Y. Ju, New fluorescent rhodamine hydrazone chemosensor for Cu (II) with High selectivity and sensitivity, Org. Lett. 8 (2006) 2863–2866.
- [31] X.T. Chen, Z.F. Lia, Y. Xiang, A.J. Tong, Salicylaldehyde fluorescein hydrazone: a colorimetric logic chemosensor for pH and Cu (II), Tetra. Lett. 49 (2008) 4697–4700.
- [32] X.F. Yang, X.Q. Guo, Y.B. Zhao, Development of a novel rhodamine-type fluorescent probe to determine peroxynitrite, Talanta 57 (2002) 883–890.
- [33] V. Dujols, F. Ford, A.W. Czarnik, A long-wavelength fluorescent chemodosimeter selective for Cu (II) Ion in water, J. Am. Chem. Soc. 119 (1997) 7386–7387.
- [34] The national standards in people's republic of china, The determination of Cr(VI) in water-diphenylcarbazine photometry, GB1467–1487.