



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

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### 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  $1.0 \times 10^{-8}$  to  $3.0 \times 10^{-7}$  M ( $0.42\text{--}12.6 \text{ ng mL}^{-1}$ ) with a correlation coefficient of  $R^2 = 0.9989$  ( $n = 10$ ) and a detection limit of  $1.5 \times 10^{-9}$  M ( $0.063 \text{ ng mL}^{-1}$ ). 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

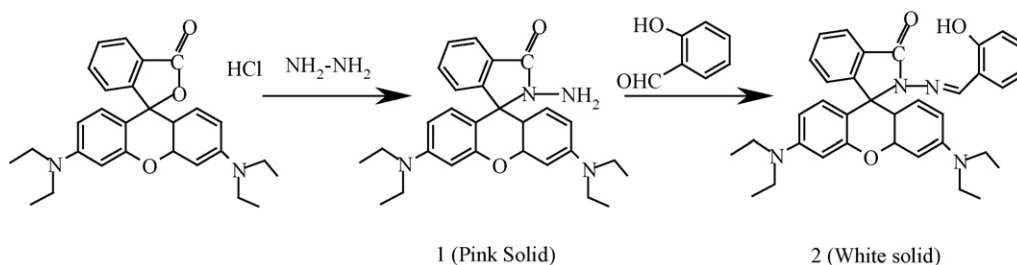
Chromium (Cr) exists in different oxidation states in the ground-water, seawater, and soil of our environment [1]. Trivalent Cr is an essential trace element in the human body as a part of the glucose tolerance factor and also plays an important role in lipid and protein metabolism. However, hexavalent 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),  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , relatively non-toxic Cr (III) [4] and another pollutant As (V) [5,6]. But Cr (VI) was found in two forms such as  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  in the water matrix. As our well known,  $\text{CrO}_4^{2-}$  is stable in neu-

tral and alkaline environments, while  $\text{Cr}_2\text{O}_7^{2-}$  in acidic conditions. Alternately, the  $\text{CrO}_4^{2-}$  can convert into  $\text{Cr}_2\text{O}_7^{2-}$  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  $\text{CrO}_4^{2-}$  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  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  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 (Tokyo, 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 JNMCA300 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),  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$  and  $\text{H}_2\text{O}_2$  were prepared from  $\text{K}_2\text{CrO}_4$ ,  $\text{NaAsO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{NaNO}_2$ ,  $\text{KMnO}_4$ ,  $\text{KClO}_3$ ,  $\text{KBrO}_3$ ,  $\text{KIO}_3$  and 30%  $\text{H}_2\text{O}_2$ , respectively. The solutions of other metal ions were prepared from their nitrate or chloride salts. Stock solutions of chromium (VI),  $\text{H}_2\text{SO}_4$ , and rhodamine B hydrazide were prepared as follows: first, Cr (VI) stock solution ( $1.00 \times 10^{-3}$  M): in a 100 mL standard flask, Cr (VI) stock solution ( $1.00 \times 10^{-3}$  M): in a 100 mL standard flask, 14.7 mg potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and 19.4 mg potassium chromate ( $\text{K}_2\text{CrO}_4$ ) was dissolved in 5 mL water, and then diluted to the mark respectively. Second,  $\text{H}_2\text{SO}_4$  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, salicylaldehyde rhodamine B hydrazide stock solution in DMF ( $1.00 \times 10^{-3}$  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%  $[\text{M}+\text{H}]^+$ ), 567.1 (5%  $[\text{M}+\text{Na}]^+$ );  $\text{M}^+$  calculated 544.3.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.15 (t, 12H,  $\text{NCH}_2\text{CH}_3$ ,  $J = 7.1$  Hz), 3.31 (q, 8H,  $\text{NCH}_2\text{CH}_3$ ,  $J = 7.1$  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,  $\text{N}=\text{C}-\text{H}$ ).  $^{13}\text{C-NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  (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  $\text{H}_2\text{SO}_4$  buffer. Typically, to a reaction solution containing 10 mM  $\text{H}_2\text{SO}_4$  buffer and  $1 \times 10^{-7}$  M SRBH, an appropriate volume of sample solution with a final Cr (VI) concentration of not more than  $1 \times 10^{-7}$  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  $\lambda_{\text{ex}}/\lambda_{\text{em}} = 520/591$  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  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-5}$  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 hydrazide (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  $\text{H}_2\text{SO}_4$  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

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