Research Article

Surfactant Sensitized Calix[4]arenes Fluorescence Quenching Method for Speciation of Cr(VI)/Cr(III) in Water Samples

Wenjun Wang, Xiashi Zhu, and Chaoguo Yan

College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou 225009, China

Correspondence should be addressed to Xiashi Zhu; xszhu@yzu.edu.cn

Received 3 June 2013; Accepted 6 July 2013

Academic Editors: L. Charbonnière, R. E. Santelli, M. Soylak, and A. R. Türker

Copyright © 2013 Wenjun Wang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The surfactant sensitized spectrofluorimetry for speciation of chromium (Cr(VI)/Cr(III)) was developed. The analytical procedure was that the fluorescence intensity of 14,10,16,22-tetramethoxyl resorcinarene carboxylic acid derivatives (TRCA) could be selectively quenched by Cr(VI) and the fluorescence quenching value ($\Delta F = F_{\text{TRCA}} - F_{\text{Cr(VI)-TRCA}}$) was increased in cetyltrimethylammonium bromide (CTAB). The main influence factors on the fluorescence quenching (ΔF) were investigated in detail. Under the optimal conditions, the linear range of calibration curve for the determination of Cr(VI) was 0.10~5.00 $\mu\text{g/mL}$, and the detection limit was 0.024 $\mu\text{g/mL}$ with RSD = 2.10% ($c = 1.0 \mu\text{g/mL}$, $n = 3$). The concentration of Cr(III) was calculated by subtracting Cr(VI) from the total chromium determined after oxidizing Cr(III) to Cr(VI). The preliminary sensitized mechanism was discussed with the inclusion constant (K) of TRCA-Cr(VI), the fluorescence quantum yield of TRCA, and IR spectra characterization. The method has been applied to the speciation analysis of Cr(VI)/Cr(III) in water samples.

1. Introduction

Chromium (Cr) is one of the most commonly present heavy metal pollutants in industrial wastewater. Chromium compounds mainly exist in two oxidation states (Cr(III) and Cr(VI)) in the environment. The reduced form of chromium Cr(III) is less toxic and is an essential nutrient required for normal glucose metabolism at low concentrations. Cr(VI) is much more mobile, toxic, and carcinogenic than Cr(III), which is widely used in electroplating, leather tanning, metal finishing, photography and dye and textile industries. The effluents from these industries often contain elevated levels of Cr(VI). Therefore, there is a great risk of chromium leaching from these effluents into the environment and our food chain. The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) recommend that the concentration of Cr(VI) in drinking water should be less than 0.05 mg L^{-1} and 0.1 mg L^{-1} , respectively [1–5]. Hence, the development of accurate and reliable methods for the speciation of Cr(III)/Cr(VI) in water samples is of particular significance to obtain comprehensive information about their toxicity and human health relevance.

A variety of analytical methods such as ultraviolet visible absorption spectrometry (UV-Vis) [6], electrothermal atomic absorption spectrometry (ETAAS) [7], flame atomic absorption spectrometry (FAAS) [8–11], high performance liquid phase chromatography (HPLC) [12, 13], inductively coupled plasma mass spectrometry (ICP-MS) [14, 15], and gas chromatography (GC) [16] were developed for the determination of Cr(III)/Cr(VI). However, most of these methods usually needed multiple separation and preconcentration steps due to their poor sensitivity and selectivity for the extremely low concentration of chromium species in complicated matrix samples. So, a simple, rapid, and efficient sample preparation method is a need for the speciation analysis of Cr(III)/Cr(VI) in water samples.

Surfactants are used in spectroscopic analysis due to their sensitization, solubilization, stabilization, growth, and contrast increasing characteristics. In our previous publications, the sensitizing effects of surfactant on the determination of metal ions by UV-Vis spectrophotometry and spectrofluorimetry were developed [17–19]. But CTAB sensitized fluorescence quenching method of the derivatives of calix[4]arene for the analysis Cr(VI)/Cr(III) seems to be lacking.

FIGURE 1: Structure of TRCA.

As the same as crown ethers and cyclodextrins, calixarene is one of the members of supramolecular host compounds: they are often used as scaffolds onto which these functional groups can be attached. They can be readily functionalized through the phenolic groups or directly on the aromatic ring, and this has resulted in the design and synthesis of a variety of derivatives for a wide range of functions [20]. In recent years, calixarenes have an extensive application in analytical chemistry for their particular construction [21–24]. The special modified functional group (carboxyl) could enhance water solubility of the calixarene, which showed highly selective recognition function and has been applied in biological molecules analysis [25]. The recognition of Cr based on host-guest chemistry of the derivatives of calix[4]arene has been reported [26, 27]. In this paper, a new type of calixarene carboxylic acid derivative was synthesized (Figure 1). The interaction of Cr(VI) and 4,10,16,22-tetramethoxyl resorcinarene carboxylic acid derivatives (TRCA) was investigated with fluorescence spectroscopy. The fluorescence quenching method of TRCA for the analysis Cr(VI)/Cr(III) has been established. There are many advantages for this method, such as quick, simple, efficient, and high selectivity, so it has a high application prospect.

2. Experimental

2.1. Apparatus and Chemicals. The fluorescence analysis was carried out by F-4500 fluorescence spectrophotometer (Hitachi, Japan); UV2550 spectrophotometer (Hitachi, Japan) and Bruker Tensor 27 infrared spectrometer (Bruker Company, Germany) were used to explore the mechanism of inclusion formation; A pHs-25 type pH meter (Shanghai Precision kore magnetic Factory) was used to control the pH value of sample solutions.

The preparation of calixarene carboxylic acid is based on the synthetic route depicted in Figure 2. 4,10,16,22-Tetramethoxyl[4]resorcinarene **2** was prepared by the previously described methods [28–30], whereas the tetramethoxyl[4]resorcinarene derivatives **3–4** were first synthesized in this work. The structure information and purities of these compounds were confirmed by TLC, FT-IR, and NMR. A stock solution of TRCA (8.5×10^{-5} mol/L) was prepared in ethanol.

The stock solution of Cr(VI) (1.00 mg mL^{-1}) was prepared by dissolving 0.2829 g $\text{K}_2\text{Cr}_2\text{O}_7$ (Shanghai Reagent Factory, Shanghai, China) in double distilled water and diluting to 100 mL. A 1.00 mg mL^{-1} stock solution of Cr(III) was prepared by dissolving 0.1000 g metallic chromium powder (Tokyo, Japan 5N) in appropriate concentrated hydrochloric

acid and diluting to 100 mL with double distilled water. Standard solutions of Cr(III) and Cr(VI) were prepared by appropriate dilution of the stock solutions, respectively.

5.0% hexadecyl trimethyl ammonium bromide (CTAB), 5.0% Triton X-100, 5.0% dodecyl sulfate sodium (SDS), 1.0% $\text{C}_{14}\text{mimBr}$ and $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$, $\text{NH}_3 \cdot \text{H}_2\text{O}-\text{NH}_4\text{Cl}$ buffer solutions were employed.

All chemicals were of analytical grade.

2.2. Procedure

2.2.1. Measuring of Fluorescence Intensity. A quantitative reference substance solution of Cr(VI), 1.0 mL $\text{NH}_3 \cdot \text{H}_2\text{O}-\text{NH}_4\text{Cl}$ buffer solution (pH = 9.0), 2.0 mL TRCA (8.47×10^{-5} mol/L), and 0.5 mL 5.0% CTAB were added in a 5.0 mL centrifuge tube. The mixed solution was diluted to final volume with distilled water and was shaken thoroughly. The obtained solution was thermostated at $30.0 \pm 1^\circ\text{C}$ for 30 min, and the fluorescence intensity of the solution ($F_{\text{Cr(VI)-TRCA-CTAB}}$) was measured at excitation wavelength 280 nm and emission wavelength from 250 to 400 nm in a 1.0 cm quartz cell by a F-4500 fluorospectrophotometer, and the fluorescence intensity of the blank solution ($F_{\text{TRCA-CTAB}}$) was measured at the same time. Then the fluorescence quenching value ΔF ($\Delta F = F_{\text{TRCA-CTAB}} - F_{\text{Cr(VI)-TRCA-CTAB}}$) was obtained. The excitation and emission bandwidths were both set to 5 nm. The scan rate is 1200 nm/min.

2.2.2. The Benesi-Hildebrand Method. In this experiment, the Benesi-Hildebrand method [31] (double reciprocal plot) was used for calculating the inclusion constant (K) of TRCA-Cr(VI) assuming a 1:1 inclusion model. And the expression was given by (1), where $[\text{TRCA}]_0$ was the total concentration of TRCA, ΔF was the fluorescence quenching value, and α was constant. Thus, the inclusion constant (K) of the 1:1 complex, which had been calculated by dividing the intercept by the slope of the double reciprocal plot:

$$\frac{1}{\Delta F} = \frac{1}{(K \cdot \alpha \cdot [\text{TRCA}]_0)} \cdot \frac{1}{[\text{Cr(VI)}]} + \frac{1}{(\alpha \cdot [\text{TRCA}]_0)} \quad (1)$$

2.2.3. Determination of Relative Fluorescence Quantum Yield [32, 33]. Fluorescence quantum yields of TRCA and TRCA-CTAB were measured using 0.1 mg/mL L-tryptophan as reference material. Under the same apparatus conditions, according to (2), the quantum yields of the analyte were calculated. Briefly, Y_s and Y_u are the corresponding standard and measurement-needed fluorescence quantum yield, and F_s and F_u the integral areas of two calibration fluorescence emission curves, A_s and A_u the absorbance ($\lambda_{\text{absorbance}} = \lambda_{\text{emission}}$) of the standard and measurement-needed materials, and $Y_s = 0.14$ (25°C) is known:

$$Y_u = Y_s \times \frac{F_u}{F_s} \times \frac{A_s}{A_u} \quad (2)$$

FIGURE 2: The synthetic routing of calixarene carboxylic acid.

2.2.4. Preparation of Water Sample. The lake water from the slender west lake (Yangzhou, China) was collected in polyethylene bottles. All water samples were filtered through 0.45 μ m pore size membrane filters immediately and then stored at 4.0°C in polyethylene volumetric flasks.

The certified reference water samples for the total chromium (GBW(E) 080462, Shanghai Institute of Measurement and Testing Technology, Shanghai, China) and the Cr(VI) (GSBZ50027-94, Institute for Environmental Reference Materials of Ministry of Environmental Protection, Beijing, China) were diluted appropriately with double distilled water.

3. Results and Discussion

3.1. Choice of Media. The fluorescence quenching values (ΔF) of Cr(VI)-TRCA ($\Delta F = F_{\text{TRCA}} - F_{\text{Cr(VI)-TRCA}}$) in different medium were investigated (Table 1). As could be seen in Table 1, the order of ΔF was

$$\Delta F_{5.0\% \text{CTAB}} > \Delta F_{5.0\% \text{SDS}} > \Delta F_{1\% \text{C}_{14}\text{mimBr}} > \Delta F_{\text{H}_2\text{O}} > \Delta F_{5.0\% \text{Triton X-110}} \quad (3)$$

The fluorescence emission spectra of TRCA (present of or absent of Cr(VI)) in CTAB and H₂O media were shown in Figure 3. It could be seen that the fluorescence intensity of TRCA (F_{TRCA}) was enhanced in presence of CTAB ($F_{\text{TRCA-CTAB}}$) (curve 3, curve 1), and the $\Delta F_2 = F_{\text{TRCA-CTAB}} - F_{\text{Cr(VI)-TRCA-CTAB}}$ (curve 1/curve 2) was larger than that $\Delta F_1 = F_{\text{TRCA}} - F_{\text{Cr(VI)-TRCA}}$ (curve 3/curve 4) with the same concentration of Cr(VI): there was the sensitizing

TABLE 1: Effect of different mediums on fluorescence intensity.

Medium	ΔF
H ₂ O	50.9
5. 0% Triton X-100	15.0
5.0% SDS	135.3
5.0% CTAB	150.4
1% C ₁₄ mimBr	92.6

effect in CTAB. Hence, 5.0% of CTAB medium was chosen for this paper.

3.2. Fluorescence Spectra. The fluorescence emission spectra of TRCA, TRCA-Cr(VI), and TRCA-Cr(III) were shown in Figure 4. It could be seen that (1) the fluorescence intensity of TRCA (F_{TRCA}) was diminished when Cr(VI) interacted with TRCA (curve 3); (2) the F_{TRCA} remained unchanging when Cr(III) mixed with TRCA (curve 2); (3) the F_{TRCA} was gradually decreased with an increase of Cr(VI) concentration (auxiliary Figure 4, curve 1–7), and curve 7 was the fluorescence spectrum of TRCA-Cr(VI) when Cr(VI) was excessive, which indicated that inclusion complex of TRCA-Cr(VI) was a weak fluorescent complex.

3.3. Optimization of Conditions

3.3.1. Effect of pH. The influence of pH on the fluorescence quenching value (ΔF) was investigated (Figure 5). As could be seen in Figure 5, ΔF was gradually enhanced and reached

FIGURE 3: Fluorescence spectra (1: TRCA, 2: TRCA-Cr(VI), 3: TRCA-Cr(III)).

FIGURE 4: Fluorescence spectra. (1) TRCA (3.4×10^{-5} mol/L) + CTAB; (2) Cr(VI) ($1.00 \mu\text{g/mL}$) + TRCA (3.4×10^{-5} mol/L) + CTAB; (3) TRCA (3.4×10^{-5} mol/L) + H_2O ; (4) Cr(VI) ($1.00 \mu\text{g/mL}$) + TRCA (3.4×10^{-5} mol/L) + H_2O .

the maximum (pH = 9.0) then remained relatively constant after pH = 9.

In order to discuss the influence of pH on ΔF , the change of $F_{\text{TRCA-CTAB}}$ and $F_{\text{Cr(VI)-TRCA-CTAB}}$ with pH was investigated (auxiliary Figure 5). As could be stated in auxiliary Figure 5(1) both $F_{\text{TRCA-CTAB}}$ and $F_{\text{Cr(VI)-TRCA-CTAB}}$ were increased with pH value (pH = 5.0 – 9.0), but $F_{\text{TRCA-CTAB}}$ had a larger changing tendency ($\Delta F \uparrow = F_{\text{TRCA-CTAB}} \uparrow - F_{\text{Cr(VI)-TRCA-CTAB}} \uparrow$); (2) $F_{\text{TRCA-CTAB}}$ and $F_{\text{Cr(VI)-TRCA-CTAB}}$ had the same changing tendency, namely, ΔF remained unchanging (pH = 9.0 – 11.0). Above all, $\Delta F_{\text{pH 9.0-11.0}} > \Delta F_{\text{pH 5.0-9.0}}$. Thus, 1.0 mL $\text{NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution of pH = 10.0 was chosen for the determination.

FIGURE 5: Effect of pH on fluorescence intensity. $C_{\text{Cr(VI)}}$: $1.00 \mu\text{g/mL}$ C_{TRCA} : 3.4×10^{-5} mol/L.

FIGURE 6: Effect of the amount of TRCA on fluorescence intensity. $C_{\text{Cr(VI)}}$: $1.00 \mu\text{g/mL}$ C_{TRCA} : 8.5×10^{-5} mol/L.

3.3.2. Effect of TRCA Amount. The effect of the amount of TRCA on the ΔF was tested. The results were shown in Figure 6. The fluorescence quenching value (ΔF) was increased and reached a maximum value at a TRCA (8.5×10^{-5} mol/L) amount of 2.0 mL and then decreased with the concentration of TRCA. Auxiliary Figure 6 shows the influence of TRCA amount on $F_{\text{TRCA-CTAB}}$. It was clear that $F_{\text{TRCA-CTAB}}$ or ΔF gradually decreased with the increase of TRCA amount due to the self-quenching of TRCA at higher concentrations. Thus, 2.0 mL TRCA (8.5×10^{-5} mol/L) was chosen for the assay.

3.3.3. Effect of CTAB Amount. The effect of the amount of 5.0% CTAB on the ΔF was investigated. As was shown in Figure 7, ΔF reached a maximum with 0.4 mL of 5.0% CTAB added and was kept constant in the CTAB volume range of

FIGURE 7: Effect of the amount of CTAB on fluorescence intensity. $C_{Cr(VI)}$: $1.00 \mu\text{g/mL}$ C_{TRCA} : $3.4 \times 10^{-5} \text{ mol/L}$.

FIGURE 8: Effect of the amount of H_2O_2 . ($C_{Cr(III)}$: $1.00 \mu\text{g/mL}$ C_{TRCA} : $3.4 \times 10^{-5} \text{ mol/L}$).

FIGURE 9: Double reciprocal plot of Cr(VI) in TRCA. (C_{TRCA} : $3.4 \times 10^{-5} \text{ mol/L}$).

FIGURE 10: The IR spectra (1: TRCA; 2: TRCA-Cr(VI)).

FIGURE 11: The configuration of inclusion (TRCA-Cr(VI)).

0.4–1.0 mL. In this work, 0.5 mL 5.0% of CTAB was chosen for the following experiments.

3.3.4. Effect of Temperature and Time. The effects of temperature ($10\text{--}50^\circ\text{C}$) and time ($0\text{--}50 \text{ min}$) on ΔF were tested. It was found that ΔF was steady ranging from 20 to 40°C and 25 to 50 min . Therefore, the suitable temperature of $30 \pm 1^\circ\text{C}$ and preparation time of 30 min were recommended for the work.

3.4. Effect of Foreign Substances. The effects of the different foreign substrates were discussed on the determination of the $1.00 \mu\text{g/mL}$ of Cr(VI). The results were shown in Table 2. It was observed that most of the common metal ions and dye molecules did not influence the determination of Cr(VI).

3.5. Effect of H_2O_2 Amount. The total chromium was determined after oxidizing Cr(III) to Cr(VI). The appropriate oxidant was (1) quantitatively oxidize Cr(III) to Cr(VI); (2) there was no quenching effect for the fluorescence intensity of TRCA. In this paper, 0.1% H_2O_2 was chosen as oxidant. So, the oxidation rate of Cr(III) and the effect of H_2O_2 on the fluorescence intensity of TRCA were investigated (Figure 8). As could be seen in Figure 8 that (1) F_{TRCA} was decreased when the amount of 0.1% H_2O_2 was 0.2 mL ; (2) the oxidation ratio exceeded 95% and was almost constant when the amount of 0.1% H_2O_2 , was more than 0.1 mL . So, 0.1 mL 0.1% of H_2O_2 was chosen for the oxidation of $1.00 \mu\text{g/mL}$ Cr(III).

TABLE 2: Effect of interfering substances on fluorescence.

Foreign ions	Foreign/Cr(VI) (w/w)
Na ⁺	500.00
K ⁺	500.00
NH ₄ ⁺	300.00
Mg ²⁺	200.00
Cu ²⁺	10.00
Zn ²⁺	10.00
Ca ²⁺	10.00
Ni ²⁺	10.00
Cr ³⁺	3.00
Pb ²⁺	2.00
Cd ²⁺	2.00
Hg ²⁺	1.00
Cl ⁻	500.00
Br ⁻	500.00
Ac ⁻	300.00
CO ₃ ²⁻	200.00
SO ₄ ²⁻	200.00
NO ₃ ⁻	100.00

3.6. Analytical Performance. Under the optimum conditions, the linear regression equation was $\Delta F = 15.39 + 288.68c$ ($\mu\text{g/mL}$) with a correlation coefficient of $R = 0.9966$. A linear relationship was observed over the range of 0.10~5.00 $\mu\text{g/mL}$. The detection limit estimated ($S/N = 3$) was 0.024 $\mu\text{g/mL}$, RSD was 2.1% ($n = 3$, $c = 1.00 \mu\text{g/mL}$).

3.7. Sample Analysis. In order to verify the feasibility of the method, the proposed method was successfully applied to the determination of Cr(III) and Cr(VI) in reference water samples (GSBZ50027-94 and GBW(E)080642) and real water samples (laboratory water samples). As could be seen in Tables 3 and 4, the determined values were in good agreement with the certified values, and the relative recoveries in the range of 102.0%–103.0% were obtained by determination of spiked real samples.

3.8. Discussion of Mechanism

3.8.1. The Interaction of TRCA and Cr(VI). TRCA is an easy-to-select modification of both the upper and lower edges, with the benzene ring units composed of hydrophobic cavities, which have a truncated cone structure which could tie with ionic object or pack neutral molecules [28]. This special molecular structure could include guest molecule (Cr(VI)) which had matched polarity, size, shape, and property into their hydrophobic cavities to form inclusion complexes, which may affect the fluorescence intensity of TRCA.

According to the Benesi-Hildebrand method, it was found that the double reciprocal plot of TRCA-Cr(VI) had good linear relationships (Figure 9), which could support the formation of a 1:1 complex, and the inclusion constant

K for Cr(VI) was $7.29 \times 10^3 \text{ L/mol}$. The larger the value of K , the more steady the inclusion complex. While, the same method was applied to investigate the interaction of TRCA and Cr(III), the results indicated that there was no interaction between them.

3.8.2. IR Spectra Characterization. From Figure 10 (curve 1: TRCA, curve 2: TRCA-Cr(VI)), carbonyl peak (1728 cm^{-1}) of TRCA disappeared and new peaks appeared at about 1683 cm^{-1} , which proved that Cr(VI) was interacting with the carbonyl of TRCA. Therefore, the reasonable configuration of interaction of TRCA and Cr(VI) may be shown in Figure 11.

3.8.3. The Sensitizing Effect of CTAB. Generally speaking, it was demonstrated that the sensitizing effect of CTAB on spectrofluorimetry rested on two factors: (1) the solubilization capacity and (2) the microenvironment of medium [34]. In order to discuss the influence of the microenvironment on the fluorescence intensity of TRCA, the fluorescence quantum yields Y_u in various media were determined, respectively (Table 5). Y_u of TRCA in the presence of CTAB was approximately 2.0 times higher than that in the absence of CTAB. The fluorescence quantum yield was one of the mostly basic and significant parameters in all the characters of fluorescence substance [35], which represented the ability of translating absorption energy to fluorescence and was tightly related to chemical structure and microenvironment of the system [36]. The Y_u value is higher, the ability of translating absorption energy to fluorescence is stronger. What is more, $\Delta F = F_{\text{TRCA}} - F_{\text{Cr(VI)-TRCA}}$, where ΔF must increase as the increasing of fluorescence quantum yield of TRCA. Therefore, the fluorescence intensity was higher in the CTAB micelle than that in H_2O medium because the CTAB micelle could better accommodate the microenvironment. In other words, CTAB was able to decrease the self-fluorescence quenching of TRCA and the fluorescence quenching effort of the external quencher. So, CTAB had sensitizing effect on TRCA and the fluorescence quenching value (ΔF) of the Cr(VI)-TRCA system.

4. Conclusion

In this paper, the fluorescence intensity of TRCA was quenched due to Cr(VI)-TRCA to form a complex, and the fluorescence quenching value (ΔF) was increased in CTAB medium. Based on this, a novel fluorescence quenching method for the determination of Cr(VI) has been developed. In comparison with ultraviolet visible absorption spectrometry (UV-Vis) [6], flame atomic absorption spectrometry (FAAS) [8–11], this present method seems to be simpler, faster, and of lower cost with better detection limit and selectivity. To the best of our knowledge, it is the first example that involves the complexation of 4,10,16,22-tetramethoxyl resorcinarene carboxylic acid derivatives with Cr(VI).

TABLE 3: Analysis of certified reference materials (mean $\pm$ S.D., $n = 3$).

Sample	Certified value ($\mu\text{g mL}^{-1}$)			Found ($\mu\text{g mL}^{-1}$)			Total Cr recovery (%)
	Cr(VI)	Cr(III)	Total Cr	Cr(VI)	Cr(III) ^a	Total Cr	
GSBZ50027-94	0.40 $\pm$ 0.01	—	—	0.42 $\pm$ 0.01	ND	0.42 $\pm$ 0.01	105.0
GBW(E)080642	—	—	100.00 $\pm$ 5.00	24.80 $\pm$ 1.30	73.24 $\pm$ 3.04	98.04 $\pm$ 3.04	98.0

ND: not detected; ^athe concentration of Cr(III) was calculated by subtracting of Cr(VI) from the total chromium.

TABLE 4: Determination of Cr(III) and Cr(VI) in real water samples (mean $\pm$ S.D., $n = 3$).

Sample	Added ($\mu\text{g mL}^{-1}$)			Found ($\mu\text{g mL}^{-1}$)			Recovery (%)	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III) ^a	Total Cr	Cr(VI)	Cr(III)	Total Cr
Tap water	0	0	ND	ND	ND	—	—	—
	0.25	0.25	0.24 $\pm$ 0.01	0.26 $\pm$ 0.01	0.51 $\pm$ 0.01	96.0	104.0	102.0
	0.50	0.50	0.52 $\pm$ 0.01	0.51 $\pm$ 0.01	1.03 $\pm$ 0.01	104.0	102.0	103.0

ND: Not detected; ^aThe concentration of Cr(III) was calculated by subtracting of Cr(VI) from the total chromium.

TABLE 5: Y_u value of TRCA in different mediums.

Medium	Y_u
H ₂ O	0.045
5% CTAB	0.089

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (21375117, 21155001), Jiangsu Key Laboratory of Environmental Material and Environmental Engineering, and the Foundation of Excellence Science and Technology Invention Team in Yangzhou University.

References

- [1] D. G. Barceloux, "Chromium," *Journal of Toxicology—Clinical Toxicology*, vol. 37, no. 2, pp. 173–194, 1999.
- [2] A. D. Dayan and A. J. Paine, "Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000," *Human and Experimental Toxicology*, vol. 20, no. 9, pp. 439–451, 2001.
- [3] M. J. Marqués, A. Salvador, A. Morales-Rubio, and M. de la Guardia, "Chromium speciation in liquid matrices: a survey of the literature," *Fresenius' Journal of Analytical Chemistry*, vol. 367, no. 7, pp. 601–613, 2000.
- [4] K. C. Tagliari, V. M. F. Vargas, K. Zimiani, and R. Cecchini, "Oxidative stress damage in the liver of fish and rats receiving an intraperitoneal injection of hexavalent chromium as evaluated by chemiluminescence," *Environmental Toxicology and Pharmacology*, vol. 17, no. 3, pp. 149–157, 2004.
- [5] S. Kalidhasan and N. Rajesh, "Simple and selective extraction process for chromium (VI) in industrial wastewater," *Journal of Hazardous Materials*, vol. 170, no. 2-3, pp. 1079–1085, 2009.
- [6] W. Chen, G. P. Zhong, Z. D. Zhou, P. Wu, and X. D. Hou, "Automation of liquid-liquid extraction-spectrophotometry using prolonged pseudo-liquid drops and handheld CCD for speciation of Cr(VI) and Cr(III) in water samples," *Analytical Sciences*, vol. 21, no. 10, pp. 1189–1193, 2005.
- [7] A. Béni, R. Karosi, and J. Posta, "Speciation of hexavalent chromium in waters by liquid-liquid extraction and GFAAS determination," *Microchemical Journal*, vol. 85, no. 1, pp. 103–108, 2007.
- [8] R. P. Monasterio, J. C. Altamirano, L. D. Martínez, and R. G. Wuilloud, "A novel fiber-packed column for on-line preconcentration and speciation analysis of chromium in drinking water with flame atomic absorption spectrometry," *Talanta*, vol. 77, no. 4, pp. 1290–1294, 2009.
- [9] P. A. Sule and J. D. Ingle Jr., "Determination of the speciation of chromium with an automated two-column ion-exchange system," *Analytica Chimica Acta*, vol. 326, no. 1–3, pp. 85–93, 1996.
- [10] R. M. Cespón-Romero, M. C. Yebra-Biurrun, and 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," *Analytica Chimica Acta*, vol. 327, no. 1, pp. 37–45, 1996.
- [11] A. Karatepe, E. Korkmaz, M. Soylak, and L. Elci, "Development of a coprecipitation system for the speciation/preconcentration of chromium in tap waters," *Journal of Hazardous Materials*, vol. 173, no. 1–3, pp. 433–437, 2010.
- [12] A. N. Tang, D. Q. Jiang, Y. Jiang, S. W. Wang, and X. P. Yan, "Cloud point extraction for high-performance liquid chromatographic speciation of Cr(III) and Cr(VI) in aqueous solutions," *Journal of Chromatography A*, vol. 1036, no. 2, pp. 183–188, 2004.
- [13] L. L. Wang, J. Q. Wang, Z. X. Zheng, and P. Xiao, "Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples," *Journal of Hazardous Materials*, vol. 177, no. 1–3, pp. 114–118, 2010.
- [14] S. Hirata, K. Honda, O. Shikino, N. Maekawa, and M. Aihara, "Determination of chromium(III) and total chromium in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry," *Spectrochimica acta B*, vol. 55, no. 7, pp. 1089–1099, 2000.
- [15] Y. C. Sun, C. Y. Lin, S. F. Wu, and Y. T. Chung, "Evaluation of on-line desalter-inductively coupled plasma-mass spectrometry system for determination of Cr(III), Cr(VI), and total chromium concentrations in natural water and urine samples," *Spectrochimica Acta B*, vol. 61, no. 2, pp. 230–234, 2006.

- [16] T. H. Ding, H. H. Lin, and C. W. Whang, "Determination of chromium(III) in water by solid-phase microextraction with a polyimide-coated fiber and gas chromatography-flame photometric detection," *Journal of Chromatography A*, vol. 1062, no. 1, pp. 49–55, 2005.
- [17] X. S. Zhu, L. Bao, R. Guo, and J. Wu, "Determination of aluminium(III) in water samples in a microemulsion system by spectrofluorimetry," *Analytica Chimica Acta*, vol. 523, no. 1, pp. 43–48, 2004.
- [18] L. Bao, X. S. Zhu, and R. Guo, "Simultaneous determination of cobalt and nickel by microemulsion sensitization-dual wavelength spectrophotometry," *Chinese Journal of Analytical Chemistry*, vol. 2, pp. 34–38, 2006.
- [19] J. Wu, Y. Gu, and X. S. Zhu, "Determination of trace lanthanum (III) by β -cyclodextrin sensitized UV-Vis spectrophotometry," *Analytical Instrumentation*, vol. 3, pp. 47–51, 2008.
- [20] M. Tabakci, B. Tabakci, and A. D. Beduk, "Synthesis and application of an efficient calix[4]arene-based anion receptor bearing imidazole groups for Cr(VI) anionic species," *Tetrahedron*, vol. 68, no. 22, pp. 4182–4186, 2012.
- [21] I. Qureshi, M. A. Qazi, and S. Memon, "A versatile calixarene derivative for transportation systems and sensor technology," *Sensors and Actuators B*, vol. 141, no. 1, pp. 45–49, 2009.
- [22] X. P. Ding, D. B. Tang, T. Li, S. F. Wang, and Y. Y. Zhou, "A novel spectrofluorometric method for the determination of methiocarb using an amphiphilic p-sulfonatocalix[4]arene," *Spectrochimica Acta A*, vol. 81, no. 1, pp. 44–47, 2011.
- [23] R. Liu, B. C. Zhou, J. W. Zhang, C. X. Jin, and L. Lin, "Study on the interaction between 4-sulfonic calixarene and pepsin," *Northern Environment*, vol. 22, pp. 60–64, 2010.
- [24] M. Chen, T. Shang, J. Liu, and G. W. Diao, "Complexation thermodynamics between butyl rhodamine B and calix[n]arenesulfonates ($n = 4, 6, 8$)," *Journal of Chemical Thermodynamics*, vol. 43, no. 1, pp. 88–93, 2011.
- [25] M. C. Semedoa, A. Karmalia, P. D. Barataa, and J. V. Prataa, "Extraction of hemoglobin with calixarenes and biocatalysis in organic media of the complex with pseudoactivity of peroxidase," *Journal of Molecular Catalysis B*, vol. 62, pp. 97–104, 2010.
- [26] S. Alpaydin, A. O. Saf, S. Bozkurt, and A. Sirit, "Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tert-butylcalix[4]arene derivative," *Desalination*, vol. 275, no. 1–3, pp. 166–171, 2011.
- [27] M. Bayrakci, S. Ertul, and M. Yilmaz, "Synthesis of di-substituted calix[4]arene-based receptors for extraction of chromate and arsenate anions," *Tetrahedron*, vol. 65, no. 38, pp. 7963–7968, 2009.
- [28] M. J. McIldowie, M. Mocerino, B. W. Skelton, and A. H. White, "Facile lewis acid catalyzed synthesis of C4 symmetric resorcinarenes," *Organic Letters*, vol. 2, no. 24, pp. 3869–3871, 2000.
- [29] M. Klaes, C. Agena, M. Köhler et al., "First synthesis, isolation and characterization of enantiomerically pure and inherently chiral resorc[4]arenes by lewis acid cyclization of a resorcinol monoalkyl ether," *European Journal of Organic Chemistry*, no. 8, pp. 1404–1409, 2003.
- [30] M. Klaes, B. Neumann, H. Stammeler, and J. Mattay, "Determination of the absolute configuration of inherently chiral resorc[4]arenes," *European Journal of Organic Chemistry*, no. 5, pp. 864–868, 2005.
- [31] V. K. Bhardwaj, A. P. S. Pannu, N. Singh, M. S. Hundal, and G. Hundal, "Synthesis of new tripodal receptors—a "PET" based "off-on" recognition of Ag^+ ," *Tetrahedron*, vol. 64, no. 22, pp. 5384–5391, 2008.
- [32] R. F. Chen, "Fluorescence quantum yields of tryptophan and tyrosine," *Analytical Letters*, vol. 1, no. 1, pp. 35–42, 1967.
- [33] P. Wu and L. Brand, "Resonance energy transfer: methods and applications," *Analytical Biochemistry*, vol. 218, no. 1, pp. 1–13, 1994.
- [34] L. N. Ma and X. S. Zhu, "Determination of emodin by hexadecyl trimethyl ammonium bromide sensitized fluorescence quenching method of the derivatives of calix[4]arene," *Spectrochimica Acta A*, vol. 95, pp. 246–251, 2012.
- [35] B. Gao, Y. O. Feng, L. S. Zhou, and X. Ma, "Progress of inclusion property of calixarene," *Chinese Journal of Organic Chemistry*, vol. 24, no. 7, pp. 713–721, 2004.
- [36] X. S. Zhu, A. Q. Gong, and S. H. Yu, "Fluorescence probe enhanced spectrofluorimetric method for the determination of gatifloxacin in pharmaceutical formulations and biological fluids," *Spectrochimica Acta A*, vol. 69, no. 2, pp. 478–482, 2008.