Facile preparation of glutathione-stabilized gold nanoclusters for selective determination of chromium (III) and chromium (VI) in environmental water samples

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HIGHLIGHTS

- Facile and rapid preparation of fluorescent glutathione-stabilized gold nanoclusters.
- New method for selective determination of Cr(III) and Cr(VI) using GSH-Au NCs.
- The detection method possessed simplicity, high throughput, high selectivity and sensitivity.

GRAPHICAL ABSTRACT

Scheme for preparation of GSH-Au NCs (a) and application in selective determination of Cr(III) and Cr(VI) (b).

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ABSTRACT

A novel method for selective determination of Cr(III) and Cr(VI) in environmental water samples was developed based on target-induced fluorescence quenching of glutathione-stabilized gold nanoclusters (GSH-Au NCs). Fluorescent GSH-Au NCs were synthesized by a one-step approach employing GSH as reducing/protecting reagent. It was found that Cr(III) and Cr(VI) showed pH-dependent fluorescence quenching capabilities for GSH-Au NCs, and thus selective determination of Cr(III) and Cr(VI) could be achieved at different pHs. Addition of EDTA was able to effectively eliminate the interferences from other metal ions, leading to a good selectivity for this method. Under optimized conditions, Cr(III) showed a linear range of 25–3800 μg L⁻¹ and a limit of detection (LOD) of 2.5 μg L⁻¹. The Cr(VI) ion demonstrated a linear range of 5–500 μg L⁻¹ and LOD of 0.5 μg L⁻¹. The run-to-run relative standard deviations (n = 5) for Cr(III) and Cr(VI) were 3.9% and 2.8%, respectively. The recoveries of Cr(III) and Cr(VI) in environmental water samples were also satisfactory (76.3–116%). This method, with its simplicity, low cost, high selectivity and sensitivity, could be used as a promising tool for chromium analysis in environmental water samples.

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1. Introduction

Chromium is widely used in industrial processes such as metal smelting, leather tanning, electroplating and dyestuff, which can lead to the release of large amounts of chromium compounds into

natural water bodies and can therefore also contaminate drinking water systems [1]. In aqueous solutions, chromium mainly exists in two valence states; namely Cr(III) and Cr(VI). Cr(III) is considered to have low toxicity and is an essential trace element for mammals, while Cr(VI) is approximately 100 times more toxic and is considered a human carcinogen with adverse impact on human skin, stomachs, lung, liver and kidneys [1–3]. Therefore, measuring total chromium levels might not accurately reflect the environmental risk of chromium contamination.

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Therefore, selective determination for Cr(III) and Cr(VI) is necessary.

Over the past decades, various techniques for determination of Cr(III) and Cr(VI) have been developed, including electro-thermal atomic absorption spectroscopy (ETAAS) [4,5], spectrophotometry coupled with cloud point extraction [6] or solid phase extraction [7] or high-performance liquid chromatography [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9,10], and inductively coupled plasma mass spectrometry (ICP-MS) [11]. However, most of these methods involve complex and time-consuming sample pretreatment procedures, and can only directly detect one valence state. Additionally, instruments such as ICP-OES and ICP-MS are bulky and expensive with high operating cost. Therefore, developing simple methods for selective and sensitive determination of Cr(III) and Cr(VI) is still a great challenge.

Recently, advances in synthesis and application of gold nano-clusters (Au NCs) as fluorescence probes have drawn wide attention due to their ultra-small size, large Stokes shift, low toxicity, strong fluorescence and long term stability [12]. These Au NCs have been successfully used in the determination of various heavy metals such as Hg(II) [13], Fe(III) [14], As(III) [15], Cu(II) [16] and Pb(II) [17] with advantages of being simple, rapid and economical. Glutathione (GSH) can be used as an environment friendly reducing/protecting reagent for Au NCs [12] and have shown a certain affinity for chromium [18–21]. Thus it is possible to use glutathione-stabilized gold clusters (GSH-Au NCs) as a fluorescent probe for selective determination of Cr(III) and Cr(VI).

In this work, a facile one-step synthesis method of fluorescent GSH-Au NCs was developed. The as-prepared GSH-Au NCs exhibited orange-red emission at 710 nm with a quantum yield (QY) of 1.5%. Speciation analysis of Cr(III) and Cr(VI) using GSH-Au NCs were achieved by varying the pHs of sample solutions due to pH-dependent fluorescence quenching capabilities of Cr(III) and Cr(VI). To the best of our knowledge, this is the first report on the application of fluorescent Au NCs for selective determination of Cr(III) and Cr(VI).

2. Experimental

2.1. Instruments

Fluorescence measurements and UV/vis absorption spectra were conducted with a Thermo Scientific Varioskan Flash Multi-mode Reader using 96-well fluorescence plates (Vantaa, Finland). The TEM images were taken by a TECNAL G2 20 electron microscope (Tokyo, Japan). The pH values were tested using a Thermo Scientific Orion® 3-Star Plus pH Benchtop Meter (Singapore).

2.2. Materials

Ethylenediaminetetraacetic acid (EDTA), rhodamine 6G, gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and NaOH were obtained from Sangon Biotech (Shanghai, China). L-Glutathione reduced ($\geq 98.0\%$) was purchased from Sigma (St. Louis, USA). 0.1 M Tris-HCl solution (pH 7.4) was purchased from Solarbio (Beijing, China). All of the metal salts were purchased from Beijing Chemical Works (China). Stock solutions of Cr(III), Cr(VI), Pb(II), Cu(II), Cd(II), Fe(III), Co(II), Ni(II), Zn(II) and Mn(II) (100 mM) were prepared in water. The standard solutions used for calibration were prepared by gradually diluting the stock solutions in water, with concentration range from 0 to $13,000 \mu\text{g L}^{-1}$ for Cr(III) and $0\text{--}1300 \mu\text{g L}^{-1}$ for Cr(VI). Deionized water from a Milli-Q Millipore with a resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was used. The pHs of solutions were adjusted by HCl or NaOH solutions. All chemicals and reagents used in this work

were of analytical grade or higher purity without further purification.

2.3. Preparation and purification of GSH-Au NCs

GSH-Au NCs were synthesized by chemical reduction of HAuCl_4 with glutathione. A solution of glutathione (5 mL, 15 mM) was added to an equal volume of 10 mM HAuCl_4 . The mixture was vigorously stirred for 2 min, followed by the addition of 1 M NaOH (1 mL). Then, the solution was incubated at 37°C under continuous stirring (ca. 200 rpm) for 24 h. Excess glutathione were thereafter removed by addition of excessive methanol into the aqueous solution (the ratio between water and methanol is 1:4) and the solution was then centrifuged at 15,000 rpm for 5 min. The precipitates were separated and finally dispersed in Tris-HCl solution for use.

2.4. Detection of Cr(III) and Cr(VI) by using GSH-Au NCs at different pHs

The detection of Cr(III) and Cr(VI) using GSH-Au NCs was conducted according to the scheme shown in Fig. 1. Cr(III) was directly detected at pH 6.5 where the relative fluorescence intensity of GSH-Au NCs were dependent on its concentration. Cr(VI) was quantified based on the difference between relative fluorescence intensities of GSH-Au NCs at pH 3.5 and 5.0. In addition, the effects of other metal ions such as Pb(II), Cu(II), Cd(II), Fe(III), Co(II), Ni(II), Zn(II) and Mn(II) on the fluorescence intensities of GSH-Au NCs at different pHs were tested to evaluate the selectivity of this method.

The detailed detection procedures were as following: the standard solutions ($49 \mu\text{L}$) were firstly mixed with $1 \mu\text{L}$ of EDTA (125 mM) in a 96-well plate for 10 min, followed by addition of $50 \mu\text{L}$ of GSH-Au NCs solution. The mixed solution was allowed to reaction for 30 min at appropriate pHs. Finally, the fluorescence intensity of the solutions was recorded from 550 to 800 nm with the excitation wavelength at 410 nm. The whole process was carried out at room temperature.

2.5. Feasibility test with real environmental water samples

Tap water and effluent water samples were used to evaluate the feasibility of the method. Effluent water samples were collected from Qinghe wastewater treatment plant in Beijing. All the water samples analyzed were filtered through a Millipore cellulose membrane ($0.45 \mu\text{m}$) and analyzed as described above.

3. Results and discussion

3.1. Synthesis and characterization of GSH-Au NCs

In this work, we prepared fluorescent GSH-Au NCs by a one-step method via reduction of gold salt with glutathione as both reducing and protecting agent. Molar ratios of GSH to Au, pH and reaction time were optimized. At a given Au NCs concentration of 10 mM, the optimal concentration of GSH was found to be 15 mM, in which Au NPs showed the which Au NCs showed the strongest fluorescence (Fig. S1A in the Supporting Information). The appropriate pH was 11.5 (Fig. S1B), and the reaction was allowed to proceed for 24 h at 37°C (Fig. S1C). In contrast to previously reported methods [16,22–24], this method is more rapid, which could be the effect of higher temperature. The higher pH could also be more beneficial to the reducing ability of glutathione, similar as the behavior of bovine serum albumin [25]. In addition, smaller nanoparticles could be formed at higher pHs due to stronger electrostatic repulsion of the carboxylate groups in GSH between adjacent ligands [26].

Fig. 1. Scheme for preparation of GSH-Au NCs and application in selective determination of Cr(III) and Cr(VI).

Fig. 2. (A) Photographs of an aqueous solution of GSH-Au NCs in visible light (left) and UV light (right). (B) UV/vis absorption (black line), fluorescence excitation (red line, emission at 710 nm) and emission (green line, excitation at 410 nm) spectra of GSH-Au NCs.

Fig. 3. (A) Typical TEM image of GSH-Au NCs. (B) Corresponding particle size distribution histograms for GSH-Au NCs based on 200 nanoparticles.

Fig. 4. Effect of pH on the relative fluorescence (F/F_0) of GSH-Au NCs in the absence and presence of 25 μ M of different metal ions with EDTA.

The color of the as-prepared Au NCs solution was yellow under visible light and bright orange-red under UV light (Fig. 2(A)), indicating that highly luminescent species were formed. A typical absorption spectrum of the prepared GSH-Au NCs solution is shown in Fig. 2(B) (black line). Unlike the UV-vis absorption spectra of gold nanoparticles with diameter over 10 nm, the surface plasmon resonance absorption around 500 nm is lacking, indicating that the diameter of the prepared material was less than 10 nm. The maximal excitation and emission wavelengths of the as-prepared Au NCs were 410 and 710 nm, respectively (Fig. 2(B)). Such GSH-Au NCs have a large Stokes shift of 300 nm, which can avoid crosstalk between the excitation and emission signals. To further confirm the formation of GSH-Au NCs, high resolution transmission electron microscopy (HRTEM) images were obtained (Fig. 3(A)). The gold clusters are spherical in shape and well dispersed. Fig. 3(B) shows the distribution of sizes of the gold clusters (average diameter 2.4 ± 0.7 nm).

The quantum yield of luminescent GSH-Au NCs in aqueous solution (pH 7.0) was measured at $1.5 \pm 0.4\%$, using Rhodamine 6G (QY=0.95 in ethanol) as the reference. This quantum yield is approximately four times higher than that of the GSH-Au NCs synthesized by reduction with NaBH_4 [27]. The as-prepared GSH-Au NCs in 0.1 M Tris-HCl solution were stable for over 1 month, and no obvious change of the absorption and emission spectra was observed for over a week (Fig. S2). Furthermore, the high water solubility of GSH-Au NCs allows their application in aqueous media without using organic co-solvents.

3.2. Effect of pH values on Cr(III) and Cr(VI) detection

The pH is a critical parameter in selective determination of Cr(III) and Cr(VI). Results given in Fig. 4 indicated that pH had little effect on the fluorescence quenching of GSH-Au NCs in the presence of EDTA and most metal ions with the exception of Cr(III) and Cr(VI) under acidic conditions. While at the higher pH range of 8.5–11, most metal ions including Cr(III) and Cr(VI) were unstable and could not react with GSH-Au NCs. Thus, the fluorescence intensity of gold nanoclusters did not change.

At the pH range of 3.5–6.5, 25 μ M of Cr(III) ions could lead to 32–45% fluorescence quenching of 2.5 mM GSH-Au NCs (Fig. 4). The possible reasons were hypothesized as (1) under acidic condition, the Cr(III) is able to form complex with glutathione (Au NCs-GSH-Cr(III)-GSH-Au NCs) [28], resulting in the aggregation of gold clusters; (2) GSH can bind to Cr(III) via the terminal glycine group (N,O) and the deprotonated

Fig. 5. Effect of 25 μ M of different metal ions on the relative fluorescence (F/F_0) of GSH-Au NCs at pH 6.5. F_0 and F correspond to the fluorescence intensity of GSH-Au NCs in the absence and presence of 25 μ M of different metal ions with EDTA ($\lambda_{\text{ex}} = 410$ nm, $\lambda_{\text{em}} = 710$ nm).

sulphur of cysteine [18,19], which may compete with Au-S and result in the displacement of GSH from the surface of the gold clusters. The displacement of GSH capping consequently created imperfection on the material surface, thus resulting in fluorescence quenching [29].

Under acidic condition, Cr(VI) could also lead to fluorescence quenching of GSH-Au NCs (Fig. 4). The reason may be associated with the high positive redox potential of Cr(VI) at acidic pHs [30]. The redox interaction between Cr(VI) and GSH [20,21] results in the instability of Au NCs, which ultimately induce fluorescence quenching. More importantly, the fluorescence quenching capability of Cr(VI) for GSH-Au NCs was highly dependent on pHs. As shown in Fig. 4, 25 μ M Cr(VI) resulted in 99% fluorescence quenching of GSH-Au NCs at pH 1.0 and 92% at pH 3.5. However, it could only cause 10% fluorescence quenching at pH 5.0 and less than 5% at pH 6.5. This could be explained by the weaker oxidation capacity of Cr(VI) at elevated pHs [3,30]. The lower oxidizing power of Cr(VI) weakened the redox reaction between Cr(VI) and GSH which reduced fluorescence quenching of GSH-Au NCs.

Based on the results mentioned above, a stepwise strategy was designed to selectively detect Cr(III) and Cr(VI) in water samples (Fig. 1). Cr(III) was directly detected at pH 6.5 in which Cr(VI) nearly showed no fluorescence quenching capability for Au NCs. Detection of Cr(VI) was based on the difference of its relative fluorescence intensities between pH 3.5 and 5.0 in which no interferences from Cr(III) was observed because the fluorescence quenching capability of Cr(III) at those two pH values are at similar levels.

3.3. Effect of EDTA

Besides Cr(III) and Cr(VI), other metal ions present in natural water system such as Pb(II), Cu(II), Co(II) and Ni(II) could also cause fluorescence quenching of GSH-Au NCs and the potential interactions between those metals and GSH [29] might interfere with the accurate detection of Cr(III) and Cr(VI). Therefore, EDTA was added as masking ligand to improve the selectivity of the method for Cr(III) and Cr(VI) analysis. Upon addition of EDTA, the interference from other metal ions was notably reduced (Fig. S3). This may be owing to the relatively slower formation kinetics of Cr(EDTA) complex which have much weaker quenching effect on GSH-Au NCs [31]. The fluorescence quenching capabilities of various heavy metal ions in the presence of different amount of EDTA were further studied. The results indicated with the addition of EDTA, the fluorescence

Fig. 6. $F/F_{0(\text{pH } 5.0)} - F/F_{0(\text{pH } 3.5)}$ values in the absence and presence of 25 μM of different metal ions with EDTA ($\lambda_{\text{ex}} = 410 \text{ nm}$, $\lambda_{\text{em}} = 710 \text{ nm}$).

quenching of GSH-Au NCs introduced by Pb(II), Cu(II), Co(II) and Ni(II) were decreased and 1.25 mM EDTA was appropriate for eliminating the interferences of these metal ions at concentrations up to 25 μM (Fig. S3).

3.4. Selectivity

The selectivity of the GSH-Au NCs toward Cr(III) and Cr(VI) ions was investigated in detail using above strategy. The changes of relative fluorescence intensity (F/F_0) of GSH-Au NCs occurred within 30 min (Fig. S4). F_0 and F are the fluorescence intensities of the Au NCs before and after adding metal ions, respectively. As shown in Fig. 5, at pH 6.5, addition of 25 μM of Cr(III) caused approximately 38% fluorescence quenching of GSH-Au NCs (2.5 mM) whereas addition of other metal ions including Cr(VI) at the same concentration (25 μM) led to less than 5% change, which demonstrated little interference to the fluorescence intensity of GSH-Au NCs. The results indicated that GSH-Au NCs at pH 6.5 could be a selective fluorescence probe for Cr(III) ions.

In the Cr(VI) determination, pH 3.5 and pH 5.0 was selected as working pHs. As shown in Fig. 6, other metal ions such as Cr(III), Pb(II), Cu(II), Cd(II), Fe(III), Co(II), Ni(II), Zn(II) and Mn(II) at the concentration of 25 μM did not cause strong change in the values of $F/F_{0(\text{pH } 5.0)} - F/F_{0(\text{pH } 3.5)}$. Only 25 μM of Cr(VI) ions led to almost 80%

quenching difference of GSH-Au NCs fluorescence between pH 3.5 and pH 5.0. These results indicate that this system display high selectivity toward Cr(VI) ions.

3.5. Analytical performance

To study the linearity of the method, the value of F/F_0 was monitored with a series of Cr(III) solutions. As observed in Fig. 7(A), F/F_0 of gold nanoclusters decreased linearly ($R^2: 0.9907$) with increasing concentration of Cr(III) within 25–3800 $\mu\text{g L}^{-1}$ (Fig. 7(B)). When Cr(III) concentration reached 13 mg L^{-1} , the GSH-Au NCs fluorescence was almost completely quenched.

Furthermore, Cr(VI) was also investigated with different concentrations added to GSH-Au NCs solutions at pH 3.5 and 5.0. F/F_0 of GSH-Au NCs decreased with increasing concentration of Cr(VI) at pH 3.5 (Fig. 8(A)), but no significant changes were found at pH 5.0 (Fig. 8(B)). Fig. 8(C) shows the corresponding F/F_0 of GSH-Au NCs at pH 3.5 and 5.0. From Fig. 8(D), it can be seen that the value of $F/F_{0(\text{pH } 5.0)} - F/F_{0(\text{pH } 3.5)}$ shows a good linearity ($R^2: 0.9911$) with Cr(VI) concentration within the range of 5–500 $\mu\text{g L}^{-1}$.

According to Figs. 7(B) and 8(D), the quenching behavior of the fluorescent sensors for Cr(III) and Cr(VI) in the tested concentration of 25–13,000 $\mu\text{g L}^{-1}$ and 5–1300 $\mu\text{g L}^{-1}$ all fitted the square root function of $y = b + a\sqrt{x}$ [32]. Therefore, the function was used to further evaluate the performance of the method. Results showed that the function worked very well for both target ions, which simplified the calibration process and widened the detection concentration range (as shown in Table 1).

The limit of detection (LOD) was estimated as the lowest concentration of the analyte that could be detected. The lowest detectable response was equal 3 times of the standard deviation (SD) of 7 parallel blank measurements [33]. The solution of GSH-Au NCs (2.5 mM) in the absence of metal ions was used as a blank. The SD of the blank responses was 0.15 for Cr(III) and 0.05 for Cr(VI). LODs of Cr(III) and Cr(VI) were 2.5 $\mu\text{g L}^{-1}$ and 0.5 $\mu\text{g L}^{-1}$, respectively (Table 1). The reproducibility of the method was also evaluated and the results were satisfactory (as listed in Table 1). The relative standard deviations ($n=5$) for Cr(III) and Cr(VI) were 3.9% and 2.8% for run-to-run assays, respectively. The satisfactory day-to-day RSDs, as listed in Table 1, also indicate the good stability of the GSH-Au NCs.

This method could be considered as environmentally friendly for the use of minute amount of gold nanoclusters, and compared to some fluorimetry and colorimetry methods [33–35] shown in Table 2, it gives comparable or even superior LODs and wider detection range. Compared with other methods such as ETAAS [4,5],

Fig. 7. (A) Fluorescence emission spectra of GSH-Au NCs in the absence and presence of Cr(III) with different concentration at pH 6.5. (B) Plot of the relative fluorescence (F/F_0) of GSH-Au NCs versus Cr(III) concentration. The inset shows the linear detection range for 25–3800 $\mu\text{g L}^{-1}$ of Cr(III) ($\lambda_{\text{ex}} = 410 \text{ nm}$, $\lambda_{\text{em}} = 710 \text{ nm}$).

Fig. 8. Fluorescence emission spectra of GSH-Au NCs in the absence and presence of (A) Cr(VI) with different concentrations at pH 3.5 and (B) Cr(VI) with different concentrations at pH 5.0. (C) Plot of the relative fluorescence (F/F_0) of GSH-Au NCs at pH 3.5 and pH 5.0 versus Cr(VI) concentration. (D) Plot of depreciation of the F/F_0 of GSH-Au NCs between pH 3.5 and pH 5.0 versus Cr(VI) concentrations. The inset shows the linear detection range for 5–500 $\mu\text{g L}^{-1}$ of Cr(VI) ($\lambda_{\text{ex}} = 410 \text{ nm}$, $\lambda_{\text{em}} = 710 \text{ nm}$).

Table 1

Analytical performance of the method for Cr(III) and Cr(VI) detection using GSH-Au NCs under the optimum condition.

Analyte	Regression equation	R^2 ^c	Linear range ($\mu\text{g L}^{-1}$)	LOD ^d ($\mu\text{g L}^{-1}$)	RSD (%)			
						Run-to-run ^e	Day-to-day ^f	Batch-to-batch ^g
Cr(III)	$y = 97.4 - 0.0128x^{a1}$ $y = 106.9 - 0.874\sqrt{x}^{a2}$	0.9907 0.9908	25–3800 25–13000	2.5	3.9	7.5	12.2	
Cr(VI)	$y = 2.82 \pm 0.126x^{b1}$ $y = -6.55 \pm 2.80\sqrt{x}^{b2}$	0.9911 0.9738	5–500 5–1300	0.5	2.8	9.6	13.7	

a1: linear regression; a2: square root regression. y = relative fluorescence intensity (F/F_0), x = concentration of Cr(III) ($\mu\text{g L}^{-1}$).

b1: linear regression; b2: square root regression. y = the depreciation of F/F_0 at pH 3.5 and pH 5.0, x = concentration of Cr(VI) ($\mu\text{g L}^{-1}$).

^c The coefficient of determination (R^2).

^d Limit of detection.

^e The run-to-run RSDs calculated from five parallel analyses.

^f The day-to-day RSDs calculated between 3 days with five parallel analyses per day.

^g The batch-to-batch RSDs determined from three batches of GSH-Au NCs.

Table 2

Comparison of the method with some other studies on detection of Cr(III) and Cr(VI).

Detection technique	Sample treatment	Target ions	Detection limit (detection range) ($\mu\text{g L}^{-1}$)		Ref.
			Cr(III)	Cr(VI)	
ETAAS/ICP-MS	On-line solid phase extraction with two minicolumns	Cr(VI)	–	0.003 (0.01–1)	[4]
ETAAS	Adsorption of Cr(III) with iron phosphate	Cr(III)	0.02 (0.05–2.5)	–	[5]
ICP-OES	Triton X-114 and CPB-Triton X-114	Cr(III)/Cr(VI)	0.02 (5–1500)	0.05 (10–1000)	[9]
ICP-OES	Magnetic solid phase extraction	Cr(III)/Cu(II)/Pb(II)/Zn(II)	0.035 (0.1–100)	–	[10]
ICP-MS	Chelating and anionic ion-exchange minicolumns	Cr(III)/Cr(VI)	0.03 (0.3–60)	0.009 (0.1–60)	[11]
Fluorimetry	N-amyl alcohol	Cr(VI)	–	0.47 (5.2–104)	[33]
Fluorimetry	DPC	Cr(VI)	–	1.2 (3.6–520)	[34]
Colorimetry	–	Cr(III)	52	–	[35]
Fluorimetry	EDTA	Cr(III)/Cr(VI)	2.5 (25–13000)	0.5 (5–1300)	This study

Table 3Spike recoveries of chromium ions in water samples ($n=3$) under the optimum condition.

Analyte	Tap water samples			Effluent water samples		
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Cr(III)	0	ND ^a		0	ND	
	510	509 $\pm$ 18 ^b	99.8 $\pm$ 3.5 ^c	510	388 $\pm$ 14	76.3 $\pm$ 2.7
	2500	2862 $\pm$ 259	114 $\pm$ 10	2500	2900 $\pm$ 318	116 $\pm$ 13
Cr(VI)	0	ND		0	ND	
	25	21 $\pm$ 2	89.3 $\pm$ 6.5	25	18 $\pm$ 2	77.7 $\pm$ 8.3
	250	216 $\pm$ 13	86.7 $\pm$ 5.2	250	194 $\pm$ 16	78.1 $\pm$ 6.4

^a Non-detectable.^b Mean $\pm$ standard deviation.

ICP-OES [9,10], and ICP-MS [11], this method could be considered more economical and the sample treatments are more simple. Additionally, the use of a 96-well plate instead of a colorimetric cuvette made the detection procedure simple, fast and high throughput.

3.6. Analysis of Cr(III) and Cr(VI) in real water samples

The method was applied to real water samples spiked with Cr(III) or Cr(VI) ions. Standard solutions were spiked to tap water or effluent water samples to prepare solutions with Cr(III) at 510 and 2500 $\mu\text{g L}^{-1}$ or Cr(VI) at 25 and 250 $\mu\text{g L}^{-1}$. As listed in Table 3, the recoveries ranged 86.7–114% for tap water samples and 76.3–116% for the effluent water samples. These recoveries were satisfactory, indicating that the sample matrix caused no significant interference to the detection.

4. Conclusion

Fluorescent GSH-Au NCs were synthesized via a facile one-step method. The diameters of the obtained gold clusters were smaller than 3 nm, possessing strong fluorescence with a quantum yield of $\sim 1.5\%$. Following this, a new method for selective determination of Cr(III) and Cr(VI) was developed based on the fluorescence quenching of GSH-Au NCs at different pHs. As compared to other reported methods, the method used in this study offers advantages including simplicity, good selectivity, high sensitivity, wider linear dynamic range and is relatively green and economical. Therefore, this method could have the potential to be a useful tool for selective determination of Cr(III) and Cr(VI) in environmental water samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aca.2013.01.042>.

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