Bis-pyrazolyl functionalized mesoporous SBA-15 for the extraction of Cr(III) and detection of Cr(VI) in artificial jewelry samples

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Abstract:

A new method coupling novel solid-phase extraction (SPE) with inductively coupled plasma-atomic emission spectrometry (ICP-AES) was developed, based on the adsorbent prepared by modifying a strong-coordinating bis-pyrazolyl functional monomer onto mesoporous silica SBA-15. The adsorbent **DPP@SBA-15** was characterized by a set of analytical techniques, as well as studied the optimized various experimental parameters such as pH, stripping agent, adsorption capacity and equilibrium adsorption time. This

newly developed adsorbent material do exhibit good chemical and mechanical stability, satisfactory adsorption capacity (72.5 mg/g) and high selectivity for Cr(III). Consequently, the **DPP@SBA-15** was utilized as SPE adsorbent for adsorption of Cr(III) and determination of Cr(VI). An excellent linearity was shown in the range of 1-20 $\mu\text{g/mL}^{-1}$ ($R^2=0.9999$), and the limit of determination 0.028 $\mu\text{g/mL}^{-1}$. Furthermore, Cr(VI) released from artificial ring was successfully detected and considerable recoveries varying from 97.6 to 103.0% were attained.

Graphical abstract

Keywords: Functionalized SBA-15, Solid-phase extraction, Chromium, Separation, Selective detection

1 Introduction

In view of the growing concern for environmental pollution control, the investigation and determination of heavy metals in a variety of matrices are highly demanded nowadays [1]. Chromium is one of important pollutants, which exists predominantly in terrestrial surface and aqueous environment as hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] [2]. A trace level of the Cr(III) is regarded as an essential

nutrient while Cr(VI) is carcinogenic and mutagenic in nature, as well as known to cause allergic dermatitis [3,4]. Metallic fashion accessories such as artificial rings, earrings, necklaces with prolonged and persistent skin contact, are significant origins of metal exposure for human, which potentially lead to dermatitis [5,6]. Consequently, the accurate and facile determination of Cr(VI) in jewelry plays a greatly important part in our daily life.

Various modern analytical techniques include inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and flame atomic absorption spectrometry (FAAS) are used in the determination of chromium, but can only detect the total amount of chromium [7-9]. To realize the specific determination of Cr(III) or Cr(VI), the coupling of instrumental techniques and solid-phase extraction (SPE) have been widely investigated. The separation of Cr(III) and Cr(VI) by SPE is conducted by the selective adsorption of functionalized adsorbent, which possessed high preconcentration and flexibility characters [10,11]. For example, Cr(VI)-ammonium pyrrolidine dithiocarbamate (APDC) modified multiwalled carbon nanotubes [12], Cr(III)-pyrrolidinedithiocarbamate polymer [7], Cr(III)-imprinted polymeric beads [13]. However, the adsorption capacity and contacting time remain to be raised to higher levels.

Nowadays mesoporous silica materials have been applied for the separation and preconcentration of heavy metals, due to their high surface area and mechanical stability. Furthermore, their surfaces can be functionalized and modified with different functionalities for different purposes [14,15]. Various functional monomers such as amine, tetrazole, imidazole and thioether have been modified on mesoporous silica for the strong adsorption of different metal ions e.g. Pb(II), Zn(II), Cd(II), Cu(II) and Hg(II) [16-20]. For the separation of Cr(III) and Cr(VI), different N-containing functional monomers such as amine [21,22], aminopropyl, imidazole and triazole groups [23] grafted on mesoporous silica adsorbents, displaying satisfactory selectivity and efficiency. So we

envisioned a functionalized mesoporous SBA-15 may lead to an effective SPE material for separation of Cr(III)/Cr(VI), based on its selective adsorption property, for the determination of trace hexavalent chromium.

In this study, a *N, N'*-bidentate ligand with a bis-pyrazol-functional group, having a strong coordination ability was initially prepared and successfully attached to SBA-15. This modified mesoporous material was characterized by various analytic techniques. Both static and dynamic sorption experiments were performed to evaluate the adsorption capacity and kinetics for the selective sorption of Cr(III) under controlled pH conditions, effects of interfering ions were also systematically investigated. In addition, recyclability of this adsorbent material from aqueous solutions was also performed. Finally, the adsorbent material was successfully applied in SPE to rapidly detect hexavalent chromium released from artificial rings.

2 Experimental Section

All of chemicals, materials and apparatus can be found in the Supporting Information.

2.1. Preparation of **DPP@SBA-15**

2.1.1 Synthesis of **DPP**

The synthesis method was adapted according to literature reported method [24]. Neat pyrazole (2.00 g, 29.4 mmol) was added to NaH (0.71 g, 29.6 mmol) to stirred in THF for 30min, and then SOCl₂ (1.07 mL, 1.75 g, 14.7 mmol) was added in one portion (1.8 g, 14.7 mmol). After stirring for 5 min, pyridine (11.88 mL, 11.64 g, 147.2 mmol) were added and the resulting cloudy reaction mixture was heated to reflux overnight. Distilled water (50 mL) was added and the aqueous phase extracted into CH₂Cl₂ (3 × 50 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and the filtrate was evaporated to dryness in vacuo. The crude oily product was dissolved in EtOAc and the solution evaporated to dryness in order to remove residual pyridine. The

insoluble brown solid was isolated by filtration and dried under dynamic vacuum. Then recrystallized to get a pale yellow powder Yield: 1.8 g (51%).

2.1.2 Synthesis of **DPP@SBA-15**

The method was carried out as follows: 1 mmol of **DPP** was dissolved in tetrahydrofuran and 1 mmol dehydrated K_2CO_3 was added to the solution. After 2 hrs, 1 mmol TEPIC was added into the reaction mixture drop by drop. The whole mixture was refluxed at 65 °C for 10 hrs, followed by the addition of SBA-15 (590 mg). The solvent was drained under vacuum and then resulting solid was repeatedly washed with methylene chloride and was dried to get a white solid material.

2.2 Adsorption performance

2.2.1 Adsorption experiment

The effect of pH was carried out by studying the extraction efficiency of the adsorbent in sample solutions containing 5 mg/L Cr(III), Cr(VI), respectively, at different pH values (2-8) which were adjusted by 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH. In all experiments, the material concentration was kept constant at 5 mg/20 mL. The adsorption capacity of **DPP@SBA-15** for Cr(III) and Cr(VI) in aqueous solution was investigated, respectively. 5 mg of **DPP@SBA-15** was dispersed in 20 mL aqueous solutions containing different contents of Cr(III) and Cr(VI) (5-50ppm) at the optimal pH values, respectively. All of above mixtures were continuously bath oscillated for 30 min at 25 °C, centrifuged, filtrated, the concentrations of the Cr(III), Cr(VI) in upper solutions were measured by ICP-AES, respectively.

In a meanwhile, experiments were conducted to determine the adsorption rate of Cr(III) from water samples as follows: 5 mg of **DPP@SBA-15** were dispersed in 20 mL solution containing the 30 ppm Cr(III). Each of the mixture was continuously bath oscillated at 25 °C for 10, 20, 30, 40 and 50 min. After each time period, solutions were centrifuged and filtered and determined by ICP-AES.

The extraction efficiency (E%), adsorption capacity q_e (mg/g) and q_t (mg/g) at equilibrium conditions and time t , respectively, calculated with equations displayed in Supporting Information.

2.2.2 Selectivity experiment

The selectivity of the synthesized sorbents was done by using Li(I), Na(I), K(I), Mg(II), Mn(II), Co(II), Cd(II), Ba(II), Hg(II), Pb(II), Cu(II) as interfering ions (X) individually at the same conditions: 5 mg of DPP was dispersed in 20 mL of 5 mg/L Cr(III). The experimental procedures were similar to the above adsorption experiment.

2.2.3 Reusability of **DPP@SBA-15**

The reusability of DPP@SBA-15 for Cr(III) was conducted by the adsorption-desorption experiments. Simply, 5 mg DPP@SBA-15 were added into 20 mL of 5 ppm Cr(III) standard solution (pH 6.0), then the mixture was continuously bath oscillated for 30 min at 25 °C. After determination of Cr(III) in the supernatant, the adsorbed Cr(III) on the above 5 mg DPP@SBA-15 were desorbed by 10 mL, 3mol/L HCl, then the mixture solutions were continuously bath oscillated for 30 min at 25°C. After that, the concentration of released Cr(III) in the solutions was determined as depicted above. Finally using the identical adsorbent to compete five cycles of adsorption-deposition experiments, the reusability assessment of **DPP@SBA-15** were obtained.

2.3 Application of **DPP@SBA-15** for determination of Cr(VI)

The process of hexavalent chromium released from artificial ring is as follows. We chose NaOH/Na₂CO₃ as extraction solution prepared by adding 2 g NaOH and 3 g Na₂CO₃ to 100 mL deionized water, the phosphate buffer (pH 7.0) was prepared with the help of 0.38 mol/L K₂HPO₄·3H₂O and 0.50 mol/L KH₂PO₄. Artificial ring (0.5g) was processed into debris that the diameter and the length were less than 1mm, 5mm, respectively. The prepared artificial ring debris was placed in a conical flask and added 25 mL extraction solution NaOH/Na₂CO₃, 0.5 mL phosphate buffer stirring at 90°C for

1.5 h, then cooled to room temperature and the precipitate was filtered off, the obtained filtrate diluted to 50 mL. Next, 5 mg **DPP@SBA-15** was added to 20 mL of the prepared sample solution (pH=6.0), the mixture solution was continuously bath oscillated for 30 min, centrifuged, filtrated, the obtained supernatant was determined by ICP-AES. After that, above materials were dispersed in 20 mL of 3 mol/L HCl with consecutively bath oscillating for 30 min at 25 °C to elute the adsorbed Cr(III) on DPP@SBA-15, then the supernatant was determined by ICP-AES.

Next, we choose the well-developed 1, 5-Diphenylcarbohydrazid spectrophotometric method for comparison. After pretreatment of artificial ring as above, 5 mol/L HNO₃ was added into the obtained filtrate, pH was adjusted into 7.5 ± 0.5 . Then 2.0 mL 0.5% 1,5-diphenylcarbohydrazide was added to the solution, adding the sulphuric acid to adjust pH to 2.0 ± 0.5 , and diluted to 50 mL. The content of hexavalent chromium in above solution was measured with spectrophotometric method.

3 Results and discussion

3.1 Synthesis and characterization of **DPP@SBA-15**

Fig. 1 illustrates the preparation of **DPP@SBA-15**. Initially, the **DPP** was synthesized by the reaction between 4-hydroxybenzaldehyde and pyrazole in THF solution with NaH as base. The obtained **DPP** was then used to react with 3-(triethoxysilyl)-propyl-isocyanate (TEPIC) for the preparation of triethoxysilyl-functionalized **DPP**, which was further grafted onto SBA-15 under refluxing condition in toluene to eventually synthesize the bis-pyrazolyl functionalized SBA-15 compound **DPP@SBA-15**.

(a) NaH, THF; SOCl₂; pyridine, reflux over night;
 (b) TEPIC, K₂CO₃, THF; Then SBA-15, toluene, reflux, 48 h.

Fig. 1. Synthesis of **DPP@SBA-15**.

Thermogravimetric analysis (TGA) of **DPP@SBA-15** (Fig. S1) shows the weight loss is about 13.7% from 181 °C to 637 °C, which probably due to the thermal decomposition of functional monomer modified on the surface [25,26].

In the Fourier transform infrared (FT-IR) spectra (Fig. S2) of **DPP@SBA-15** and the adsorption of Cr(III) on **DPP@SBA-15** (**Cr-DPP@SBA-15**) shows the strong absorption bands for the stretching vibrations Si–O–Si at 1088, 806 and 463 cm⁻¹. The three bands at 3408 and 1629 cm⁻¹ are assigned to bending vibration of surface Si-OH. Moreover, the adsorption bands appeared around 2936 cm⁻¹ were C-H stretching vibration of organic groups. Compared with **DPP@SBA-15**, **Cr-DPP@SBA-15** showed the band near 1558 cm⁻¹, which suggested the pyrazolyl group on **Cr-DPP@SBA-15** coordinate to metal ion [15,26,27].

The ²⁹Si CP/MAS NMR spectrum of **DPP@SBA-15** (Fig. S3A) exhibits strong signals (-100.74, -109.02 ppm) originating from structures of SBA-15 and weak signals (-17.0 ppm) derived from silyl ether groups of the crosslinker [17,28,29]. In the solid-state ¹³C CP/MAS NMR spectrum (Fig. S3B), the signals at 201.4 ppm, 118.9-161.7 ppm indicate the presence of the COO group, aromatic carbons of phenyl and pyrazolyl groups, respectively. The resonances at 23.6-77.1 ppm are designated to

aliphatic carbons, the carbon signal from the methylene group is near $\delta 77.1$ ppm [18,30,31].

Microscopy (SEM) and transmission electron microscopy (TEM) were used to research the morphology of **DPP@SBA-15**. The SEM images show that **DPP@SBA-15** possessed short rod-like structure in nano-size (Fig. 2A and B) [32], and the TEM images (Fig. 2C and D) provide the direct evidence that **DPP@SBA-15** was well-ordered hexagonal mesoporous structure [33,34]. The results suggest that the material **DPP@SBA-15** still remains the same structures as the parent SBA-15.

Fig. 2. SEM images (A and B) and TEM micrographs imaged top view (C) and inside view (D) of **DPP@SBA-15**.

The small angle X-ray powder diffraction (SAXS) pattern of **DPP@SBA-15** (Fig. S4) shows three peaks in the range of $2\theta = 0.7 - 2.0^\circ$, which are indexable as (100), (110), and (200) reflections associated with hexagonal symmetry [35,36]. The results show the preservation of the hexagonal structure of **DPP@SBA-15**, which is conformity to the microstructure obtained from TEM.

Nitrogen adsorption–desorption isotherm of **DPP@SBA-15** (Fig. 3) shows typical type IV isotherms with H1 hysteresis loop that is represented of mesoporous structure,

the volume adsorption of isotherm increased sharply in a relative pressure (P/P_0) range from 0.6 - 0.8, further illustrating the mesoporous structures were well maintained. The physical parameters of SBA-15 and **DPP@SBA-15** were summarized in Table S1. After functionalization, the total pore volume decrease from 0.87 to 0.51 cm^3/g , with obviously reduce of the BJH average pore diameter from 7.8 to 7.4 nm, which due to the functional monomer modified on SBA-15 [37,38].

Fig. 3. N_2 adsorption-desorption isotherms and pore size distribution (inset) of **DPP@SBA-15**

3.2 Adsorption performance

3.2.1 Effect of pH

The pH value of aqueous solution is one of most important parameters for adsorption process, which could affect species of Cr(III) and Cr(VI) existing in solution [15]. The influence of pH (2.0 - 8.0) on extraction efficiency of Cr(III) and Cr(VI) were shown in Fig. 4A. There is no great difference for adsorption between Cr(III) and Cr(VI) when pH was less than 4.0. Moreover, the extraction efficiency of Cr(III) kept a straight increase in a pH range of 4.0-6.0, and quantitative adsorption ($>90\%$) could be got from

pH 6.0 to 8.0. However, there is still almost no adsorption for Cr(VI). The different pH trends enabled the separation of Cr(III) and Cr(VI), so a pH of 6.0 was choose as the optimal value to remove Cr(III). The results could be explained from the possible adsorption mechanism of **DPP@SBA-15** for Cr(III) by the following aspects. For Cr(III), it principally exists as complex $[\text{Cr}(\text{H}_2\text{O})_3]^{3+}$ under low pH condition. With the increase of pH, the water coordinated with Cr(III) was replaced by more reactive OH^- lead to a more labile form, for instance, $[\text{Cr}(\text{H}_2\text{O})_2\text{OH}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})(\text{OH})]^{2+}$, which may strengthen the interaction with DPP grafted on SBA-15 [39]. More importantly, nitrogen from DPP could coordinate with Cr(III), due to the empty 3d orbitals. For Cr(VI), the 3d and 4s orbitals were fully occupied by the paired election of HCrO_4^- . Cr(VI) mainly existed as CrO_4^{2-} under $\text{pH} > 3$, while the protonation of DPP was lowered, which make the adsorption of Cr(VI) also difficult [40].

3.2.2 Adsorption capacity and contact time

The adsorption capacity of an adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from a solution. Therefore, in order to evaluate the maximum adsorption capacity, adsorption capacity of **DPP@SBA-15** for Cr(III) and Cr(VI) was explored in the optimum pH 6.0 (Fig. 4B). As can be seen, the adsorption capacity of **DPP@SBA-15** for Cr(III) increased with increasing the initial concentrations of Cr(III) in the range of 5-20 ppm, and then reached a plateau within the concentration of 20–50 ppm, while Cr(VI) was almost not adsorbed. The maximum adsorption capacity of **DPP@SBA-15** for Cr(III) was up to 1.4 mmol/g (72.5 mg/g), while it did almost not adsorb Cr(VI). The adsorption capacity datum demonstrates that **DPP@SBA-15** owns superior absorption to Cr(III) than other reported materials in the Table 1.

The influence of contact time between **DPP@SBA-15** and Cr(III) were carried out (Fig. 4C). We can see that the adsorption capacity of adsorbents for Cr(III) increased sharply during the initial stage, then reached equilibrium within 30 min.

Table 1. Comparison of **DPP@SBA-15** and other SPE adsorbents

Adsorbent	Adsorbed species	q_e^a (mg/g)	Detection technique	LOD ^b (ug/L)		Reference
				Cr(III)	Cr(VI)	
NH ₂ -SBA-15	Cr(VI)	12.24	FAAS	-	0.2	[22]
3-aminopropyltriethoxy silane modified MCM-41	Cr(VI)	227.5	ETAAS	-	0.09	[41]
SBA-15@Cr(III) ion imprinted polymer	Cr(III)	131.4	DSPE-FAAS	0.06	-	[42]
APTES functionalized SBA-15	Cr(III)	38.50 ^c	ICP-AES	0.53	-	[43]
Chromium(III)-imprinted AAPTS-functionalized silica gel	Cr(III)	30.5	ICP-MS	0.004	0.008	[44]
poly(EDMA-MAH-Cr(III)) imprinted polymer	Cr(III)	69.28	FAAS	1.200	-	[13]
Chlorella Vulgaris cell	Cr(VI)	-	ETAAS	0.02	0.03	[45]
DPP@SBA-15	Cr(III)	72.5	ICP-AES	-	0.0284	This work

^a Adsorption capacity at equilibrium, ^b Limit of determination, ^c The maximum adsorption capacity.

Fig. 4. (A) Effect of initial pH on extraction efficiency of **DPP@SBA-15** for Cr(III) and Cr(VI); (B)

Adsorption isotherms of **DPP@SBA-15** at different original concentrations of Cr(III) and Cr(VI); (C) Effect of contact time on Cr(III) on to **DPP@SBA-15**; (D) Reusability of **DPP@SBA-15**.

3.2.3 Selectivity

Since natural samples may have complex matrices and non-specific background absorption caused by interfering species such as metal ions, the influence of various ions for the adsorption property of **DPP@SBA-15** was also evaluated (Table 2). At pH 6.0, most metal ions (X) have no interference and the method is selective toward Cr(III) ion. This may suggest the presented method can also be applied to various natural samples as the adsorption property of **DPP@SBA-15** is not affected by relatively high concentrations of alkaline and alkaline earth metals. Furthermore, this high selectivity of this sorbent toward Cr(III) ions could be attributed to the bis-pyrazolyl functionality attached.

Table 2. The tolerance limit of various ions on the determination of 5 ug/mL of Cr(III) ion

Interfering ions (X)	Tolerable concentration ratio X/Cr(III)	R ^a (%)
Li ⁺	1000	95.3
Na ⁺	1000	96.1
K ⁺	1000	95.4
Mg ²⁺	1000	94.6
Mn ²⁺	1000	96.5
Co ²⁺	1000	94.8
Cd ²⁺	1000	97.3
Ba ²⁺	1000	96.6
Hg ²⁺	50	95.7
Pb ²⁺	1000	96.1
Cu ²⁺	1000	95.9

^a Recovery.

3.2.4 Reusability of **DPP@SBA-15**

The influence of the types of stripping agents were tested by using various eluents including hydrochloric acid, nitric acid, thiourea and their combinations. As Table S2 shown, the optimal percentage of recovery of Cr(III) could be obtained with 10 mL of HCl (3mol L⁻¹). Additionally, the recycling experiments were performed. According to

the results presented in Fig. 4D, extraction efficiency of **DPP@SBA-15** was almost no less after 5 adsorption-desorption cycles using 5 mg **DPP@SBA-15** material. These data indicated that this functionalized SBA-15 possessed comparable adsorption property can remain active in multiple adsorption-desorption cycles.

3.3 Application of **DPP@SBA-15** for determination of Cr(VI)

With the **DPP@SBA-15** and the optimized experimental conditions in hand, further application for rapid detection of toxic Cr(VI) in artificial ring was then conducted. In this process, the artificial ring was initially broken into small pieces for further extraction. The obtained solution was then adjusted to pH 6.0 and diluted into certain amount. Next, this solution was added into the reaction tube with **DPP@SBA-15** to separate Cr(III) by adsorption. After this, the solution was then filtrated for further ICP-AES analysis.

Under the selected conditions, the analytical performances of **DPP@SBA-15** based on SPE were investigated. A remarkable linearity over concentration of Cr(VI) range from 1 to 20 ug/mL were displayed, with the regression equation of $y=0.9917x-0.0865$, ($R^2=0.9999$). The limit of determination (LOD) for Cr(VI) was calculated by three times standard deviation of ten consecutive measurements of the blank divided by the slope of calibration curve, were attained of 0.028 ug/mL, which is lower than some other reported works (Table 1). The relative standard deviation (RSD) at 1 ug/mL and 10 ug/mL was 3.46% and 2.33%, respectively ($n = 6$).

Furthermore, the method of **DPP@SBA-15**-SPE coupled with ICP-AES were applied for the determination of Cr(VI) in artificial ring. Chromium from artificial ring was extracted with NaOH/Na₂CO₃ solution, then the pH value of this solution was adjusted to 6.0. Coupling the adsorption of **DPP@SBA-15** for Cr(III) with ICP-AES, we realized the direct determination of extraction solution Cr(VI). The recoveries were in the range of 97.6% and 103.0% for Cr(VI) when different Cr(VI)/Cr(III) proportions were added into extracting solution. For comparison, we used the well-developed 1, 5-Diphenylcarbohydrazide spectrophotometric method to further evaluate the accuracy

of the newly developed method. As shown from Table 3, the determined values of the newly developed method in this work with satisfactory recoveries were well agreed with the ones of 1,5-Diphenylcarbohydrazide spectrophotometric method. Therefore, the method of **DPP@SBA-15**-SPE pretreatment procedure coupled to ICP-AES hold great potential for the rapid determination of Cr(VI) in artificial jewelry samples.

Table 3. Analytical results of **DPP@SBA-15**-ICP-AES method and 1,5-Diphenylcarbohydrazide spectrophotometric method for the determination of Cr(VI).

Sample	DPP@SBA-15 -ICP-AES method						1,5-Diphenylcarbohydrazide spectrophotometric method	
	Added(mg/L)		Found (mg/L)		Recovery (%)		Found (mg/L)	Recovery (%)
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(VI)	Cr(VI)
Ring	0.00	0.00	0.056±0.002	0.054±0.002	-	-	0.056±0.001	-
	0.00	0.50	0.055±0.002	0.569±0.009	-	103.0	0.555±0.007	99.8%
	0.50	0.50	0.564±0.010	0.550±0.016	101.6	99.2	0.597±0.017	108.2%
	5.00	0.50	5.094±0.060	0.542±0.016	100.7	97.6	0.583±0.012	105.4%

4. Conclusions

In this work, a new absorbent **DPP@SBA-15** was synthesized by grafting bis-pyrazolyl-functional groups onto mesoporous SBA-15, which possesses considerable adsorption capacity and satisfactory selectivity for Cr(III), as well as good chemical stability and reusability. Accordingly, we developed a new method which **DPP@SBA-15** was employed as SPE adsorbent for removal of Cr(III) followed by ICP-AES determination for Cr(VI). The new method with a low LOD (0.0284 ug/L), high sensitivity, good precision for the determination of Cr(VI) in aqueous solution. Furthermore, the new developed method was applied to determine Cr(VI) in artificial ring directly. Comparing with the well-established 1,5-Diphenylcarbohydrazide spectrophotometric method, this newly developed method was proved to be a quicker and more accurate process with higher efficiency than conventional spectrophotometry.

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