Preparation modified SiO$_2$ nanoparticles with diphenylcarbazone for extraction and preconcentration of trace amounts of chromium ions in food, herbal and natural water samples

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ABSTRACT

The first study on the high efficiency of nanometer-sized SiO$_2$ coated with sodium dodecyl sulfate-diphenylcarbazone as a new sorbent solid phase extraction (SPE) has been reported. For SiO$_2$ nanoparticles synthesis, two solutions were prepared: one containing TEOS and EtOH, and the other composed of ammonium hydroxide, deionized water, and EtOH. The properties of, prepared SiO$_2$ nanoparticles were characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). Sorbent with modified SiO$_2$ nanoparticles was used to preconcentrate and separate Cr(III) in rael samples. Various influencing parameters on the extraction and preconcentration of trace metal, such as pH, amount of sorbent, and concentration of the chelating agent, were studied. Under the optimized operating conditions, the sorption capacities of the modified SiO$_2$ nanoparticles for Cr were 14.0 mg.g^{-1}. With 10.0 mL sample an enrichment factor of 20 was obtained. The detection limits of this method for Cr was 1.3 µg.L^{-1} and the R.S.D.s was 2.4% (n = 10). The proposed method has been applied to the determination of Cr ions at trace levels in real samples such as rice, tobacco, orange, green pepper, black tea, honey, potato, spinach, mangosteen, tomato, strawberry, carrot, apple, kiwi, mushroom, cucumber, lettuce, tab water, well water, river water and sea water with satisfactory results.

Keywords: modified SiO$_2$ nanoparticles, Chromium, Sorbent.
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INTRODUCTION

In recent years, there is a growing interest in the determination of chemical forms of an element owing to their quite different effects on human health[1-4]. Chromium is one such element which exists mainly in the environment as two oxidation states, namely Cr(III) and Cr (VI). Cr(III) is an essential element in human body and plays an important role in the metabolism of glucose, protein and lipid, whereas Cr(VI) is detrimental to health even at relatively low levels as it may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers[5-7]. The toxicity of Cr(VI) is attributed to its ability to migrate across the cell membrane, as a result of increasing intracellular chromium concentrations[8]. Release of Cr into the environment is due to its extensive use in many technology fields ranging from electroplating, dyeing, steel, leather, wood preservation in industry to artificial fertilizers in agriculture. Therefore, it is of increasing importance to monitor the total concentration of chromium, especially the concentration of the individual chromium species.

In general, the determination of chromium species is not possible directly by instrumental methods including inductively coupled plasma atomic emission spectrometry (ICPAES), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). To solve this problem, separation and preconcentration steps are usually required prior to the determination. A number of methods such as solvent extraction, coprecipitation, ion exchange, cloud point extraction, solid phase extraction, capillary microextraction and chromatography have been reported in the literatures for speciation of chromium[9-17]. In comparison with the

methods mentioned above, solid phase extraction has become increasingly popular because of its major advantages: (i) higher enrichment factor, (ii) absence of emulsion, (iii) safety with respect to hazardous samples, (iv) ease of automation, (v) minimal costs due to low consumption of reagents, (vi) the ability to combine with different modern detection techniques[18-19].

It should be noted that the adsorbent material plays a fundamentally important role in this technique, and the development of a new adsorbent material with high selectivity and sensitivity is forever of interests to analysts. Owing to its small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties, nanostructure material as new adsorbent for preconcentration and separation of substance has drawn growing attention in analytical sciences. Some nanometer-size substances, such as multiwalled carbon nanotubes, carbon nanofibers, nanometersize TiO_2, ZrO_2, SiO_2, CeO_2, ZnO, γ-Al_2O_3, Fe_3O_4 nanoparticles and titanium dioxide nanotubes have been successfully used as solid-phase extractants for preconcentration/separation of metal and nonmetal ions[20-27], as well as adsorption of organic compounds[28].

Nanometer SiO_2 is a promising material as a solid-phase extractant because of its large specific surface area, high adsorption capacity and low temperature modification. It has been widely used to prepare complex materials and as carrier of catalyst[29]. Recently, organic groups modified nanometer SiO_2 have been reported for the separation and preconcentration of metal ions in natural samples[30-31].

MATERIALS AND METHODS

Apparatus
We applied a Thermo Flame atomic absorption spectrophotometer (FAAS) model M5AA, equipped with an air-acetylene flame as the atomizer was used for the determination of chromium. Measurements were carried out in the peak area mode at 357.9 nm, using a spectral bandwidth of 1.0 for Cr(III). The lamp currents were set at 5 mA for it. The pH values were dimensioned with a pH meter model 744 from metrohm supplied with a glass-combined electrode. Separation was relieved using a refrigerated centrifuge kokusan ensinkico model H-11N.

Reagents and solutions
All reagents were of analytical grade, unless otherwise stated. SDS (Merck, Germany) was used without more purification. The chelating solution was prepared by dissolving 0.089 g of diphenylcarbazone in 25 mL water. The stock standard solutions containing 1000 $mg.L^{-1}$ of Cr (III) was prepared by dissolving appropriate amount of chloric salt in distilled water and working standard solution was earned by appropriate stepwise dilution of the stock standard solution. SiO_2 nanoparticles was activated by shaking with 4 $mol.L^{-1}$ HNO_3 (merck, 65%) and washed three times with distilled water. HCl (merck, 37%), CH_3COOH (merck, 99%), NH_3 (merck, 27%), NaOH (merck), $CrCl_3$ (merck), K_2SO_4 (merck), $NiSO_4.6H_2O$ (merck), $Fe(NO_3)_3.9H_2O$ (merck), $Hg_2 (NO_3)_2.2H_2O$ (merck), $Ba(NO_3)_2$ (merck), $CuSO_4.5H_2O$ (merck), $ZnSO_4.7H_2O$ (merck), $MnSO_4.H_2O$ (merck), NaCl (merck) were used.

Preparation of modified SiO_2 nanoparticles
0.5 g of SiO_2 nanoparticles powder and 5 mL 4.0 $mol.L^{-1}$ HNO_3 solution was added in a 100mL flask and then the flask was shaked mechanically for 10 min. HNO_3 solution was separated using a filter and it was washed with high purity deionized water. After this step 10 mL solution containing 100 mg SDS and 1 mL diphenylcarbazone solution was added in a 100 mL flask. The pH of solution was adjusted to 2.0 with 1.0 $mol.L^{-1}$ HCl solutions, and then the flask was shaked mechanically for 10 min and then modified SiO_2 nanoparticles was separated using a filter paper.

General Producer
The solutions containing 0.1–4 $mg.L^{-1}$ Cr $^{3+}$ were prepared to insid of 20 ml erlenmeyer flasks containing 0.5 g nano-SiO_2, respectively. chromium solutions at pH value was adjusted to 9 with was used 2 ml buffer NH_3. The solid/liquid phases were separated by centrifuging at 4500 rpm. The analytes in the effluent were determined by FAAS. The SiO_2 nanoparticles could be modified repeatedly by SDS and diphenylcarbazone after each desorption step by acid.

Preparation of real samples
cucumber (2.0 g), rice (2.0 g), tabbaco (2.0 g), tomato (2.0 g), potato (2.0 g), strawberry (2.0 g), apple (3.0 g), mangosteen (2.0 g), kiwi (2.0 g), honey (2.0 g), carrot (2.0 g), green pepper (2.0 g), mushroom (2.0 g), black tea (2.0 g), lettuce (2.0 g) and orange (2.0 g) samples were digested with 10 mL of concentrated HNO_3 (65%) and 3 mL of H_2O_2 (30%). After digestion of the samples, the volume of the digested sample was made up to 25 mL with distilled water.

A 40 g spinach sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 $^{\circ}$C. The residue was cooled, treated with 10 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 3 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 9.0 made up to 25 mL.

Water samples (*i.e.* tap water, sea water, river water and mineral water) were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter and aliquots of water (10 mL) were subjected to SPE. Then the procedure given in Section General Procedure was applied.

RESULTS AND DISCUSSION

Surface morphology
The morphology and size of SiO_2 nanoparticles before coating with sodium dodecyl sulfate and diphenylcarbazone (SDS- diphenylcarbazone) are illustrated in Fig 1-2.
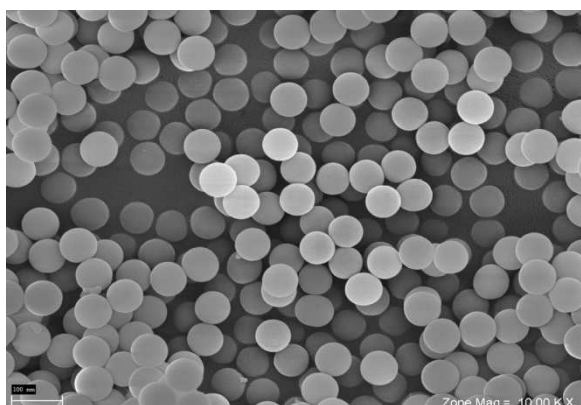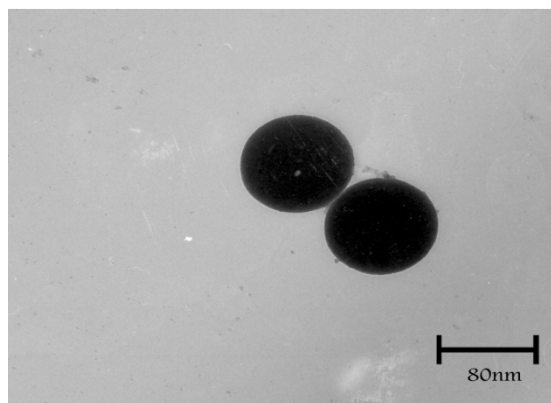

Fig 1. SEM image of SiO_2 nanoparticles

Fig 2. TEM image of SiO_2 nanoparticles

Effect of pH
The anionic surfactant SDS is effectively retained on positively charged SiO_2 nanoparticles surfaces via formation of self-aggregates over a wide pH range (1–4), whereas very little amount of SDS could be retained on inert surface of SiO_2 nanoparticles. Maximum sorption of SDS on SiO_2 nanoparticles was achieved at pH 1–2.2 by shaking the solution containing SDS and SiO_2 nanoparticles for 10 min. When solution was acidified, SDS would form hemi-micelles on SiO_2 nanoparticles by strong sorption. (Fig 3)
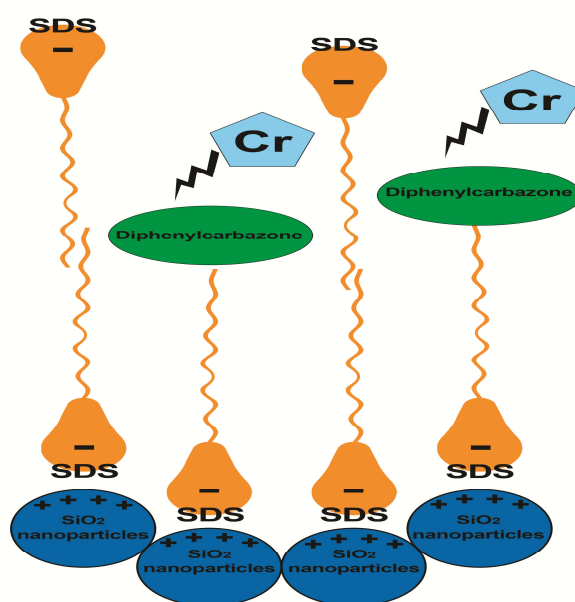

Fig 3. A suggested binding mode of SDS- diphenylcarbazone to SiO_2 nanoparticles surface

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The pH value plays an important role in the sorption of different ions on the sorbents. The sorption behavior of Cr(III) on the modified SiO_2 nanoparticles in real samples was studied in the pH range of 2.0–10.0. The pH of the solution was adjusted at the required value by the addition of 2ml buffer NH_3. According to the results, a quantitative recovery (>95%) was found for Cr at the pH range of 8–10. In order to preconcentrate ions simultaneously, a pH of 9 was selected as the compromise condition. (Fig 4)
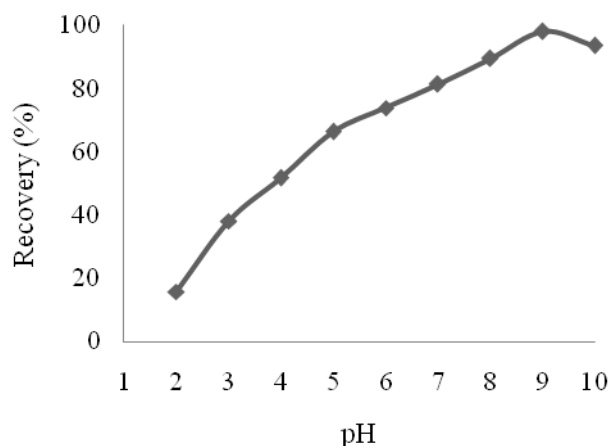
Fig 4. Effect of pH on sorption Cr on modified SiO_2 nanoparticles

Effect of the amount of modified SiO_2 nanoparticles

In order to interrogate the effect of the amount of modified SiO_2 nanoparticles on the quantitative extraction of Cr, the extraction was conducted by various the amounts of the modified SiO_2 nanoparticles from 50 to 500 mg. The results showed that the quantitative resumption (>95%) of Cr was obtained with additive of modified SiO_2 nanoparticles amount up to 400 mg.
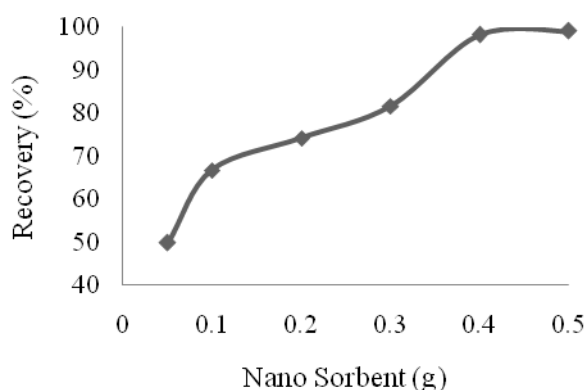
Fig 5. Effect of the amount of modified SiO_2 nanoparticles

therefore 500 mg of the modified nanometer-sized SiO_2 was used for more experiments due to the greater availability of the surface area at high amounts of the sorbent and to account for other exploitable species. (Fig 5)

Choice of recovery solvent

Some experiences were carried out in order to choose a proper solvent for the adsorbed Cr(III) ion from modified SiO_2 nanoparticles. The Cr ion was stripped with different concentrations (0.1–1 mol. L^{-1}) of various acids. From the data given in Table 1, it is obvious that 0.5 mL of 0.5 mol.L^{-1} HNO_3 could accomplish the quantitative dissolve of Cr(III) from the modified SiO_2 nanoparticles. Thus, we selected 0.5 mL of 0.5 mol.L^{-1} HNO_3 as solvent for stripping of studied metal ion.

Effect of coexisting ions

Most common matrix constituents of real samples, such as alkali and alkaline earth elements, do not react with diphenylcarbazone. However, large amounts of metal ions, which react with diphenylcarbazone, appreciably reduce the extraction efficiency of chromium.

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Table 1. Effect of type and concentration of eluent on the adsorption of Cr(III)

Eluent	Concentration $(mol\ L^{-1})$	Recovery (%)
CH$_3$COOH	1	23.7
	0.5	17.4
	0.1	12.8
H$_2$SO$_4$	1	66.9
	0.5	57.3
	0.1	42.7
HCl	1	91.3
	0.5	85.9
	0.1	77.2
HNO$_3$	1	99.2
	0.5	98.1
	0.3	91.4
	0.2	82.9
	0.1	75.4
	0.08	65.8
	0.05	59.3

Table 2. Influences of some foreign ions on the recoveries of analytes

Ion	Interferent/Cr (III) (Weight ratio)	Recovery (%)
Na$^+$	1000	98.3
K$^+$	1000	99.4
NO$_3^-$	1000	96.9
SO$_4^{2-}$	500	95.5
Cl$^-$	500	98.4
Ba^{2+}	200	97.7
Zn^{2+}	100	95.2
Mn^{2+}	50	96.3
Cu^{2+}	50	98.1
Cd^{2+}	50	95.7
Hg^{2+}	20	97.2
Fe^{3+}	10	96.6
Ni^{2+}	10	95.9

The effects of common coexisting ions in real samples on the extraction recovery of Cr(III) were studied. In these experiments, 5.0 mL of solutions containing 10 µg.L^{-1} of Cr and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered as interfering when it caused a variation in the absorbance of the analyte greater than 5%. According to the results, there is no interference from the coexisting ions in the real samples for the determination of Cr.

Method validation
Analytical figures of merit
Table 3 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, repeatability, and enrichment factor.

Table 3. Analytical characteristics of proposed method

Analytical feature	Parameter
4-580	Linear range (µg L^{-1})
1.3	Limit of detection (µg L^{-1}) (n =10)
2.4	Repeatability (RSD, %) (n =10)
20	Enrichment factor

Real sample analysis and analytical performance
This method was applied to determine of chromium in water, food and herbal samples. In order to test the applicability and reliability of the proposed method, tap water, river water, sea water, well water, rice, tobacco, orange, green pepper, black tea, honey, potato, spinach, mangosteen, tomato, strawberry, carrot, apple, kiwi, mushroom, cucumber, lettuce samples were analyzed. For this purpose, 10 mL of each of the samples were preconcentrated with modified SiO$_2$ nanoparticles, in accordance with the proposed method. The results are shown in Tables 4 and 5. In all cases the spike recoveries confirmed the reliability of the proposed method.

Table 4. Determination of Cr (III) in different water samples

Recovery (%)	Cr³⁺ detected (µg L⁻¹)	Cr³⁺ spiked (µg L⁻¹)	Sample
—	10.7 (3.2)ᵃ	0.00	Tap water
95	57.5 (2.3)	50	
97	106.9 (2.1)	100	
—	12.4 (3.2)	0.00	Sea water
96	59.9 (2.7)	50	
94	106.2 (3.4)	100	
—	not detected	0.00	River water
96	48.2 (3.5)	50	
99	99.4 (3.7)	100	
—	not detected	0.00	Well water
96	47.8 (3.3)	50	
97	96.8 (2.9)	100	

a.   RSD of three replicate experiments

Table 5. Determination of Cr (III) in food and herbal samples

Sample	Concentration (×10⁻³ mg/g)	Sample	Concentration (×10⁻³ mg/g)
cucumber	0.037 (3.5)ᵃ	Apple	0.038(2.7)
rice	0.078 (4.7)	mangosteen	0.063 (4.8)
tobacco	0.033 (2.9)	Kiwi	0.036 (3.9)
tomato	0.054 (4.1)	Orange	0.077 (4.4)
potato	0.069 (4.6)	green pepper	0.031 (2.9)
Black tea	0.020(3.7)	Honey	0.039 (3.7)
Spinach	0.028 (2.4)	Strawberry	0.035 (4.6)
Carrot	0.038 (4.5)	Mushroom	0.044 (3.1)
lettuce	0.025 (3.3)		

RSD of three replicate experiments

CONCLUSION

These results show that the ligand loaded on the modified SiO₂ nanoparticles is sensitive and accurate method for determination of trace amounts of chromium ions in low concentrations. The results presented in this paper have confirmed the applicability of the separation and preconcentration of Cr(III). The proposed solid phase extraction method is superior for having lower RSD and lower detection limits when compared to other methods and it is simple, rapid and low analysis cost. Therefore, this method should be successfully employed for determination of chromium in food, herbal and water samples by FAAS.

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