

Speciation of Cr(III) and Cr(VI) in Environmental Water Determined by Selective Separation and Preconcentration on the PBST-RSP

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Abstract—In this paper, a new method for the speciation, separation and preconcentration of Cr(VI) and Cr(III) in water was developed. The procedure presented based on two forms of chromium show different adsorption capacities on the Porous nano-barium strontium titanate by reversed-phase suspension polymerization and sol-gel method (PBST-RSP) at different pH values, that is, Cr (VI) selectively retained at pH 1–2, but Cr(III) can't be adsorbed. Whereas Cr (III) retained at pH 7-14, but Cr(VI) can't be adsorbed. Hence complete separation of the Cr(VI) and Cr(III) is possible. Retained Cr(VI) and Cr(III) were eluted with 1 mol/L HCl and 1 mol/L NaOH, respectively. The Cr(VI) and Cr(III) concentration were measured by flame atomic absorption spectrometer. The method was successfully applied for the speciation of chromium in surface water and drinking water samples with successfully results.

Keywords—Porous nano-barium strontium titanate, Speciation analysis, Chromium, Water

I INTRODUCTION

In the recently yeas, with the increase of human activities, mass of environmental pollutants are discharged into the environment, leading to serious environmental problems. Among all environmental pollutants, heavy metal ions are now catching much attention because of the remarkable toxicity. And speciation study of heavy metal ions is very important since toxicity of some of them depends on their chemical properties, oxidation states, and bioavailabilities [1]. Chromium is one of the most abundant elements having the potential to contaminate water, and so can be a major source of drinking water contamination. In water, chromium can usually be found in two different oxidation states including hydrated Cr(III) and Cr(VI) species with different physiological effects [2]. Cr(III) is a trace element essential for maintaining glucose, cholesterol, and fatty acid metabolisms in biological cells [3–5]. But Cr(VI) with a high oxidation potential and relatively small size can easily permeate through biological cell membranes, and is known as a carcinogenic and mutagenic substance for humans [3]. Due to the high solubility of Cr(VI) in water, drinking water could be one of the routes to the incorporation of chromium into the human body. The ministry of health of the people's republic of china and standardization administration of the people's republic of china has set a limit of 0.05 mg/L of chromium(VI) for drinking water[6].and The United States Environmental

Protection Agency (EPA) has set a limit of 0.1 mg/L of total chromium for drinking water. The guideline value recommended by World Health Organization (WHO) is 50 µg/L [7]. For this reason, determination of chromium in environmental samples as natural water, waste water samples and drinking water samples has become very important.

Owing to these, precise and accurate determination of both species in environmental samples is essential. The methods for determination and speciation of chromium(III) and chromium(VI) species mainly selective techniques are solid phase extraction followed by instrumental analysis [5,8,9]. But porous nano-barium strontium titanate by reversed-phase suspension polymerization and sol-gel method (PBST-RSP) sorbents has not studied. In this work, a new method using PBST-RSP as sorbent has been developed for the preconcentration and separation of Cr (III) and Cr (VI) in water.

II EXPERIMENTAL

A Apparatus and reagents

A WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co., Ltd.), equipped with hollow cathode lamps for chromium. The operating conditions were summarized in Table 1.

The pH values were measured with a PHS-3C acidometer (Shanghai REX Instrument Factory, Shanghai, China) supplied with a combined electrode.

TABLE 1. FAAS OPERATING CONDITIONS

Element	Wave length (nm)	Spectral band width (nm)	Lamp current (mA)	Burner height (mm)	Acetylene gas consumption (mL/min)	Air consumption (mL/min)
Cr	391.1	0.4	12	5.0	1250	5000

The porous nano-barium strontium titanate by reversed-phase suspension polymerization and sol-gel method (PBST-RSP) was prepared by a citric acid complex sol-gel method in our laboratory as previously described elsewhere [10].

The reagents, Cr(NO₃)₃, HCl and NaOH was guarantee reagent, K₂Cr₂O₇ was primary reagent. Stock standard

solutions of Cr (III) and Cr (VI) were prepared by dissolving appropriate amount of $\text{Cr}(\text{NO}_3)_3$ in 0.5 mol/L HCl and $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. The water in this study was distilled water.

B General separation and preconcentration procedure

A specific amount of Cr(III) and Cr(VI) solution was placed into a 50 mL calibrated mark erlenmeyer flask with plug. Solutions were adjusted to a pH 12-13 in the case of preconcentration of Cr (III) in the mark erlenmeyer flask 1 and to pH 1 in the case of preconcentration of Cr (VI) in the mark erlenmeyer flask 2. The preconcentration of investigated species was then performed simultaneously. 0.1 g of PBST-RSP was added. Covered with a plug, shaken for 10 min in a bath shaker (200r/min). Then the supernatant fluid was poured out. Sorbed Cr (III) and Cr (VI) ions were desorbed with 5mL of 1 mol·L⁻¹ HCl and 1 mol·L⁻¹ NaOH, respectively. Eluted samples were analyzed with atomic absorption spectrometry, the absorption and preconcentration capacity was calculated.

C Influence of pH on adsorption of Cr (III) and Cr (VI)

Differences between sorption energies of Cr (III) and Cr (VI) on the PBST-RSP surface provide the main reason for their selective preconcentration on the surface. Results concerning the effect of pH on the adsorption are presented in Fig.1, and it is apparent that pH >7 is appropriate for the preconcentration of Cr (III) on GBST. The quantitative recovery of Cr (VI) is obtained at pH values ≤ 2. Depending on the pH, GBST can then selectively adsorb Cr(III) or Cr (VI), this makes PBST-RSP a very promising solid phase extractant in the chromium speciation analysis.

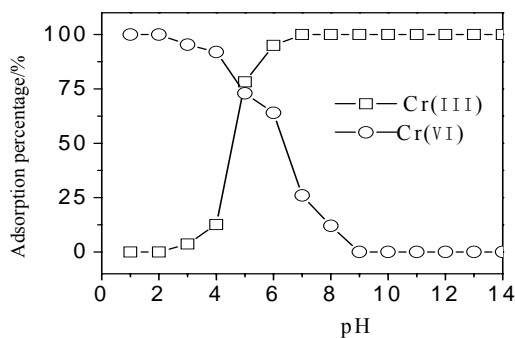


Figure 1. Effect of pH on the adsorption

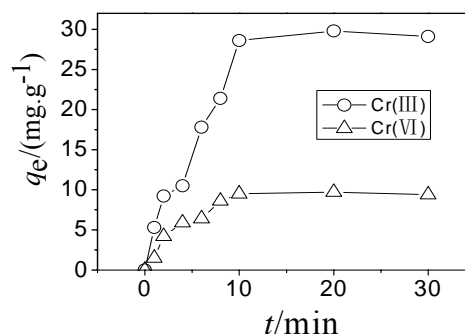


Figure 2. Effect of shaking time on adsorption

D Effect of contact time

At room temperature, the adsorption capacities for Cr (III) and Cr (VI) were determined with different shaking times (Fig.2). The results indicate that the adsorption capacity increased with an increase in shaking time and reached equilibrium more than 10 min. Therefore, the shaking time was 20 min in this study.

E Adsorption capacity

According to Fig.2, at room temperature, the static adsorption capacities of SGCTO to Cr (III) and Cr (VI) were 29.8 mg/g and 9.7 mg/g, respectively.

F Elution conditions

Fig.1 shows that the adsorption of Cr (III) at pH ≤ 2 and Cr (VI) at pH ≥ 9, could be negligible. So, after the Cr (III) and Cr (VI) were adsorbed under the optimized adsorption conditions. Elution of Cr (III) and Cr (VI) from PBST-RSP surface, by HCl and NaOH, respectively, at different concentrations and volumes was investigated. Recovery was quantitative (>95%) with 5mL 1 mol/L NaOH and 5mL 1 mol/L HCl for Cr (VI) and Cr(III), respectively.

After elution, the PBST-RSP was dried and reused 20 times. Its adsorption performance did not decrease, indicating that this adsorption agent was very stable.

G Effect of coexisting ions

The influences of possible matrix ions in the environmental samples and some transition metals were also examined. So various interference ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , $\text{Mn}(\text{VII})$, Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Al^{3+} , $\text{Mn}(\text{II})$, Co^{2+} and Fe^{3+} , were added into 50 mL volumetric flask containing 0.25 μg of Cr(VI) and Cr(III). The recovery of heavy metal ions were determined according to experimental method with the error controlled within $\pm 5\%$. The results showed that in the presence of 1000 mg·L⁻¹ Na^+ , K^+ , 500 mg/L Mg^{2+} , Ca^{2+} , $\text{Mn}(\text{VII})$, 200 mg/L $\text{Mn}(\text{II})$, Zn^{2+} , 50 mg·L⁻¹ Al^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} and Fe^{3+} . The recoveries of the analytes were still above 95%. It can be seen that the presence of major cations had no obvious influence on the recovery under the selected conditions.

H Application to the real samples

The proposed method was applied to the separation, preconcentration and determination of Cr (III) and Cr (VI) in environmental water samples. The water samples were filtered through a 0.22 μm membrane filter and analyzed

immediately. The analytical results and the associated recovery are given in Table 2. The recoveries were 93.1% - 97.5% for Cr(III) and 94.5% - 102.3% for Cr(VI), which are excellent for trace analysis.

TABLE 2. RESULTS FOR THE DETERMINATION OF Cr(III) AND Cr(VI) IN THE WATER SAMPLES

Samples	Found (mg/L)		Added (mg/L)		Recovered (mg/L)		Recovery percentage (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water	0.0082	0	0.1	0.1	0.1071	0.0937	98.9	93.7
River water	0.0124	0.0136	0.1	0.1	0.1161	0.1128	103.7	99.2
Lake water	0.1150	0.0171	0.1	0.1	0.2105	0.1146	95.5	97.5

III CONCLUSIONS

The reversed-phase suspension polymerization and sol-gel method (PBST-RSP) was used for separation and preconcentration of Cr(III) and Cr(VI). Two forms of chromium showed different exchange capacities at different pH values, viz. Cr (III) selectively retained at pH 7–14, whereas Cr (VI) retained at pH 1-2. Hence complete separation of the two forms of chromium was possible. Retained species were eluted with 5mL of 1 mol/L HCl and 1 mol/L NaOH. The method has been applied to the preconcentration and separation for flame atomic absorption spectrometric determinations of Cr(III) and Cr(VI) in environmental water samples with satisfied results.

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