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Solid Phase Extraction of Trace Amount of Vanadium (V) by Nanometer-sised Zirconium Dioxide

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Abstract: A new and simple method using nanometer-sized ZrO_2 as a solid phase extractant coupled with spectrophotometry was proposed for determination of trace vanadium. The nanometer-sized ZrO_2 was prepared through sol-gel method. The adsorption behavior of nanometer-sized ZrO_2 towards V (V) was investigated by spectrophotometry, and the adsorption pH curve, adsorption capacity were obtained. It was found that the fraction of adsorbed V(V) was more than 98.5% under pH 4.0, and 0.4 mol L^{-1} NaOH was sufficient for complete elution. Nanometer-sized ZrO_2 possesses a significant capacity (48.4 mg g^{-1}) for the adsorption of V (V) that is higher than that of those commonly used extractant, such as silica and nanometer-sized TiO_2. The fraction of V (V) absorbed on recycled nanometer-sized ZrO_2 still reached quite a high level, which showed that the nanometer-sized ZrO_2 was reusable in practice. The study on interference of co-existing ions indicated that ZrO_2 had high selectivity for vanadium ions. The method was applied to preconcentration of trace vanadium (V) in water samples with satisfactory results.

Keywords: Nanometer-sized ZrO_2; Adsorption; Vanadium; Preconcentration

1 Introduction

Vanadium is an important element in human bodies. Research has shown that vanadium complexes exhibit some properties similar to that of trypsin both in vivo and in vitra. It can stimulate the absorption of glucose, the synthesis of hepatin and the decomposition of glucose oxidase through ferment in fat and osteal muscle. It can also reduce the absorption of food. Vanadium has many potential applications for the treatment of diabetes [1], making determination of trace vanadium an important task.

Common methods for the determination of vanadium (V) ion include atomic absorption spectrometry [2] and spectrophotometry [3]. Unfortunately, the sensitivity of these methods is usually insufficient for the detection of very low concentration of vanadium (V) in environmental samples. In recent years, methods for determination of trace vanadium normally base on catalytic kinetic spectrophotometry [4] have been developed. Although these methods have higher sensitivity, the reaction conditions are critical and the selectivity is poor. Consequently, a preconcentration and matrix elimination step is usually required. Widely used technique for the separation and preconcentration of trace amounts of vanadium is liquid-liquid extraction [5], coprecipitation [6], ion exchange and solid phase extraction (SPE) [7].

Solid phase extraction (SPE) is a kind of sample pretreating technique, which is developed from the combination of liquid-solid extraction and column liquid chromatography. SPE has many advantages, such as simple operation, high enrichment factor, no pollution to environment, high selectivity and easiness to combine with other instruments. There have some literature reporting the use of alumina [8], active carbon [9], silica gel [10] and nanometer-sized TiO_2 [11] as adsorbents for SPE.

Nanometer-sized materials are meant clusters of atoms or molecules ranging in size from 1nm to almost 100 nm. Nanometer-sized material is a new functional material with many special properties [12]. One of the properties is that, according to the decrease of particle diameter, the surface energy and surface binding energy increase notably. Thus, the surface atoms can easily bind with other metal ions through electrostatic force. Therefore, nanometer-sized material has strong adsorbing power against many metal ions and can reach the adsorption equilibrium in a quite short time, meanwhile, nanometer-sized material has larger adsorption capacity than other materials because of its higher specific surface area so that it is considered as a kind of perfect adsorbent for

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solid phase extraction. Nowadays, nanometer-sized material used as adsorbent in solid phase extraction is mainly nanometer-sized TiO_2, Compared with nanometer-sized TiO_2, nanometer-sized ZrO_2 is more stable, more easily synthesized, and has a larger adsorption capacity for vanadium(V). According to our knowledge, up to now, no systematic study of the adsorption characteristics of nanometer-sized ZrO_2 and its application in preconcentration trace of vanadium (V) has been performed.

The aim of this work is to synthesize and characterize nanometer-sized ZrO_2, to study the adsorption characteristics of V (V) on nanometer-sized ZrO_2 under static conditions, to optimize the conditions for preconcentration of trace V (V) and to propose a new method using nanometer-sized ZrO_2 coupled with spectrophotometry for the determination of trace amount of V (V) in water samples.

2 Expermental

2.1 Instrumentation and Reagents

UV-1601 (Shimadzu co., Japan), TEM 100-CXII transmission electron microscope (Electron co., Japan), SA3100 surface area analyzer (Beckman Coulter co., U.S.A.).

Stock solution of vanadium (V) (1.0g L^{-1}) ; 1,2-cyclohexanediaminetetraacetic acid (DCTA): 0.1 mol L^{-1} aqueous solution; cetyltrimethylammomium bromide(CTA): 0.1mol L^{-1} aqueous solution; HAc-NaAc buffer solution(pH = 4.0) ; 4-(2-pyridylazo) resorcinol (PAR): 0.02% aqueous solution; $Zr(NO_3)_4 \cdot 10H_2O$. All reagents used were of analytical reagent grade. Doubly distilled deionized water was used throughout.

2.2 Preparation of nanometer-sized zirconium dioxide

10 mL of 0.1 mol L^{-1} CTA was added in 80 mL boiling water and 10 mL of 0.1 mol L^{-1} Zr $(NO_3)_4$ was slowly added drop wise. The solution cooled and pH value was adjusted to 4.2, then vaporized till remaining volume was about 30 mL, which was transmitted to a pot and heated below 500℃ for 3 h. The product was triturated into powder for use. The average particle diameter determined by TEM was 20～30 nm and the specific surface area, being analyzed with BET, was 14 m^2 g^{-1}.All these data were the average values of three parallel determinations.

2.3 Adsorption, elution and determination of sample

A 5.0 mL solution containing 5.0 μg V (V) was added to a beaker, the pH value of the solution was adjusted to be neutral with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NH_3, and then 20 mg of nanometer-sized ZrO_2 and 4.0 mL of HAc-NaAc buffer was added. The beaker was churned up on an electromagnetic stirrer for 2.5 h. After centrifugation, the concentration of the rudimental V (V) in the liquid phase was determined directly by spetrophotometry, and the amounts of the adsorbed V (V) were measured after elution with 0.4 mol L^{-1} NaOH.

The same procedure was carried out for 100 mL of the water samples containing 4.0 μg V (V) and some foreign ions.

3 Results and Discussion

3.1 Effect of pH value on adsorption

According to previous reports [13], pH value played an important role in the adsorption of metal ions on semiconductors. Adsorption of cations on amphoteric oxides such as ZrO_2 was usually accomplished only when pH value of the solution was higher than the isoelectric point (IEP) of the oxide, whereas for anion adsorption pH values lower than the IEP were required. It was, in general, postulated that the adsorption of ions on the oxide surface was preceded by participation of the surface hydroxyl groups. At a pH value higher than the IEP, the oxide surface was covered by OH^- groups and was negatively charged. As a result, the oxide became an active adsorbent of cations. The fraction of vanadium adsorbed on nanometer-sized ZrO_2 under different pH values was studied and is shown in Figure. 1. It can be seen that the adsorption rate(the fraction of vanadium(V) adsorbed) is stable within the pH value range 3.0～6.0, and a maximum adsorption rate appeared at pH 4.0. Thus, a HAc-NaAc buffer with pH 4.0 was selected for subsequent experiments. The results illustrated the possibility of nanometer-sized ZrO_2 as a very promising solid phase extractant.

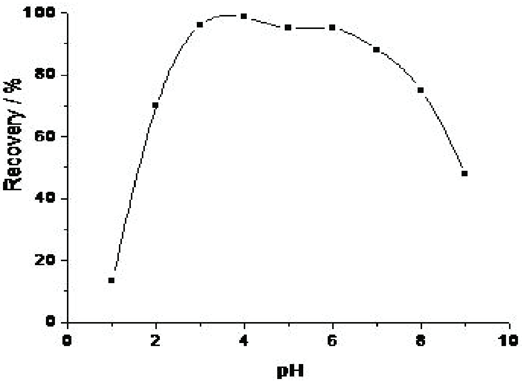

Figure 1. Effect of pH on the adsorption of V (V) on nanometer-sized ZrO_2 under static conditions. V (V): 0.5 mg L^{-1}, Sample volume: 10 mL, Nanometer-sized ZrO_2: 20 mg

3.2 Effect of the amount of nanometer-sized ZrO_2

In order to investigate the optimum amount of nanometer-sized ZrO_2 on the quantitative adsorption of vanadium(V), the adsorption of vanadium(V) ion was conducted by varying the amount of nanometer-sized ZrO_2 from 0 to 25 mg .The results showed that the adsorption rate of vanadium(V) is great than 95% at about 10 mg of nanometer ZrO_2. Thus, 20 mg of nanometer-sized ZrO_2 was chosen in our experiments.

3.3 Elution conditions

It can be seen in Figure.1 that the adsorption rate was very low in both alkaline and strong acidic media, suggesting these conditions may be suitable for elution. To choose the eluent, we tested HCl, H_2SO_4, HNO_3, HAc and NaOH with varying concentrations. The results indicated that NaOH was the most suitable eluent, and 4.0 mol L^{-1} NaOH was sufficient for complete elution. It was then found that increasing temperature was propitious to the elution and could help to shorten elution time as well as reduce the consumption of eluent. Under 98℃, the eluent concentration was optimized. The results are shown in Table I. As can be seen, 0.4 mol L^{-1} NaOH was taken for the elution.

Furthermore, the effect of elution time on the recovery of adsorbed V (V) was studied. It was found that, under 98℃, with 0.4 mol L^{-1} NaOH, when the elution time was longer than 15 min, the recovery of adsorbed V(V) was higher than 95%.

Hence, the elution was performed with 0.4 mol L^{-1} NaOH for 20 min under 98℃.

Table I Effect of NaOH concentration on the recovery of adsorbed V (V) [a]

NaOH(mol L^{-1})	0.01	0.1	0.2	0.3	0.35	0.4	0.5	0.6	0.8
% Recovery [b]	0.2	11.4	46.7	92.0	95.1	99.3	99.5	99.0	101

a Initial samples contained 5.0 μg V(V) in 10 mL solution.
b Values are averages based on three replicate analysis.
Eluting temperature: 98℃(boiling water bath) Elution time: 20 min

3.4 The adsorption performance of recycled nanometer-sized ZrO_2

After elution, the recycled nanometer-sized ZrO_2 was filtered and rinsed with 0.1 mol L^{-1} NaOH and then washed with water. The filtrate and the filter paper were transferred to a porcelain pot and dried below 105℃, then burned in a muffle furnace for 0.5 h below 500 ℃.Subsequent experiments followed the same procedure that was described in the experimental section. The adsorption rate of vanadium on the recycled nanometer-sized ZrO_2 was determined and the results are shown in Table II. From the Table we can see that the adsorption rate was still high on recycled nanometer-sized ZrO_2, indicating that the nanometer-sized ZrO_2 is reusable in practice. In contrast, according to the reference [7], the nanometer-sized TiO_2 was not reusable.

Table II The recovery of V (V) on the recycled nanometer-sized ZrO_2 [a]

Recycling times	1	2	3	4	5
% Recovery [b]	98.4	98.7	99.2	99.0	99.2

a Initial samples contained 5.0 µg V(V) in 10 mL solution.
b Values are averages based on three replicate analyses.

3.5 Analytical performance

To determine the static adsorption capacity of V (V), a 50 mg portion of nanometer-sized ZrO_2 was shaken with 10 mL of an aqueous solution containing 2000 µg of V (V) under pH 4.0, the optimal condition for adsorption. After the distribution equilibrium had been reached, the concentration of V (V) in solution was determined by spectrophotometry. The results showed the static adsorption capacity of the nanometer-sized ZrO_2 was 48.4 mg V (V) g^{-1}, which is higher than that of both silica and nanometer-sized TiO_2, the most commonly used extractant.

The break-through volume was tested by dissolving 5.0 µg of V (V) in 10, 25, 50, 100, 150, 200 and 250 mL of water and the recommended procedure was followed. The results showed that the extraction of vanadium (V) by the nanometer-sized ZrO_2 was found to be quantitative when the volume of added water was smaller than 150 mL. Thus, the break-through volume for the method should be 150 mL.

The effects of several cations on the SPE were studied. With the amount of nanometer-sized ZrO_2 and vanadium (V) fixed at 20 mg and 5.0 µg respectively, different amount of ions were added to the system, and the interferences of those ions on the extraction were studied. The results indicated that the tolerance of these ions was quite high except for Mo^{6+}, $Cu^{2+}$and Fe^{3+}, or in another word, most ions do not interfere the determination of vanadium. The interference of Mo^{6+}, Cu^{2+} and Fe^{3+} are related to competitive adsorption and can be eliminated by adding DCTA or increasing the dosage of nanometer-sized ZrO_2.

In order to assess the applicability of the method to real samples with different matrices containing varying amounts of ions, it was applied to the separation and recovery of vanadium (V) ions from the water samples. The results are shown in Table III. As can be seen, the recovery of added vanadium (V) ions in water samples was satisfactory.

4 Conclusion

Under pH 4.0 vanadium (V) was quantitatively adsorbed on nanometer-sized ZrO_2. The adsorption rate was 98.5% and the adsorption capacity was 48.4 mg vanadium (V) g^{-1}. The break-through volume was 150 mL. The adsorbed vanadium could be eluted completely by 0.4mol L^{-1} NaOH in boiling water bath. The recycled nanometer-sized ZrO_2 was reusable in practice. The study on the interference of co-existing ions indicated a high selectivity of nanometer-sized ZrO_2 for vanadium adsorption. The method was applied in analysis of vanadium (V) in water samples with satisfactory results.

Table III Recovery of V (V) in the water samples [a]

Sample	% Recovery
r sample 1 (K^+, Na^+ and Ca^{2+}, 3.0 mg of each cation)	98.7 (1.2) [b]
r sample 2 (Cd^{2+}, Zn^{2+} and Pb^{2+}, 40 µg of each cation)	96.5 (1.7)
r sample 3 (Co^{2+}, Zn^{2+} and Ni^{2+}, 40 µg of each cation)	97.2 (2.4)
r sample 4 (Al^{3+} and Cr^{3+}, 40 µg of each cation; Cr^{6+}, 4.0 µg)	95.2 (3.2)

a Initial samples contained 4.0 µg V(V) in 100 mL water.
b Values in parentheses are R.S.D.s based on five replicate analyses.

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