Sodium trititanate whisker separation/pre-concentration trace cadmium in water samples

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Abstract—The present paper proposes the application of sodium trititanate whisker as solid sorbent for trace cadmium pre-concentration/separation using a static system coupled with flame atomic adsorption spectrometry (FAAS). The method comprised the pre-concentration of Cd(II) ions at a buffered solution (pH 5.0) onto 0.25 g of sorbent previously activated by 3.0 mol/L of HNO₃. The elution step was carried out with 10 ml of 2.0 mol/L of HCl. The effect of the experimental parameters, such as sample pH, amount of sodium trititanate whisker and eluent were studied. Also, the effect of foreign ions on the determination of Cd(II) was also investigated. Under the optimum conditions, the greatest static adsorption capacity of sodium trititanate whisker for Cd(II) was 36.07 mg/g, and lower limit of detections and precision are 0.015 mg/L and 1.31%, respectively.

Keywords— Sodium trititanate whisker; Pre-concentration/separation; FAAS; Cd(II); water samper

I. INTRODUCTION

Cadmium ions are serious cumulative body poison and not easy to transform in the natural environment, which can enter our body system through air, water, and food, and cause severe damage to humans, therefore, it is of increasing importance to get rid of these heavy metal ions [1]. As the content of heavy metal ions in natural waters is normally at the low level, only a few analytical techniques are capable of removing them in water. As a result, pre-concentration and separation are required. In recent years, the methods widely used to determine micro and trace amount cadmium components are mainly involved in: solid-phase extraction [2-4], ion exchange [5], coprecipitation [6], liquid membrane enrichment [7] and so on. Attention has been paid to solid-phase extraction in the sense that it operates simply and the speed of analysis is fast, last but not least, it can unify many kinds of different examinations methods.

Different solid-phase sorbents have been used for cadmium ions pre-concentration/separation, such as ion exchangers, silica and so on. Compared with other solid-phase sorbents employed in chemistry industry, sodium trititanate whisker with larger specific surface area, which suggests a good characteristic for adsorption and elution processes, is fascinating new enrichment material, in the sense that it has special laminated structure which can be seen from Figure 1 [8-9], the inter laminar space is rather large, Most important, there are plenty of Na⁺ which are prone to be exchanged by heavy metal ions.

II. EXPERIMENTAL

A. Main apparatus and Reagents

Spectrometric measurements were carried out with a TAS-986 flame atomic adsorption spectrometer (Purchased from Beijing Purkinje General Instrument Co., Ltd, Beijing, China), the main operating conditions are shown as follows: Wavelength: 283.3 nm; Lamp current: 4.0 mA; Height of burning equipment: 8.0 mm; Narrow aperture: 0.4 nm; Flow-rate of acetylene: 2700 mL/min; Burner position: 3.0 mm; Air pressure: 0.25 MPa.

Analytical grade chemical reagents were used throughout as well as doubly distilled water. Standard stock solution of Cadmium (1 g/L) was prepared by dissolving 0.3991g of Cd(NO₃)₂ of analytical purity in nitric acid(1+49), and diluting the solution to 250 mL with nitric acid(1+49). Standard solutions was prepared by appropriate dilution with nitric acid(1+49) from the stock solution of Cadmium, immediately prior using, and the concentrations were as follows: 0.5, 1, 3, 5, 8, 10, 12 mg/L. The foreign ion solutions (1 g/L) were prepared by conventional methods.

Sodium trititanate whisker (mesh 80-200) was purchased from Shanghai Jingxu Composite manufacturing co., LTD. Prior to use, the material was dispersed in 3.0 mol/L of HNO₃ being further marinated for 24 h at room temperature. Afterwards, the material was washed with doubly distilled water.

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water until remove the excessive acid (neutral pH of solution), filtrated and dried, whetted and then sifted out with 100 mesh sifter, and stored until use.

**B. Experimental method**

A portion of sample solution containing the investigated ions was transferred to a 50 mL colorimetric cylinder. The pH value was adjusted with diluted HNO₃ and/or NaOH, and the final volume was diluted to 50 mL. Then, 0.20 g sodium trititanate whisker was added, and the solution was stirred vigorously for 5.0 min and placed for 2.0 h to facilitate adsorption of Cd(II) ions onto the sorbent, and then centrifugated. After centrifugation, the concentrations of the unadsorbed ions in the liquid phase were determined directly by FAAS, and the amounts of the adsorbed ions were measured by FAAS after elution with 10 mL of 2.0 of mol/L HCl.

### III. RESULTS AND DISCUSSION

**A. Influence of pH on adsorption**

In the solid phase studies, pH plays a very important role with respect to the adsorption of cadmium [10]. During the experiments, the influence of pH on the adsorption of Cd(II) ions were investigated. The results were shown in Fig.2. It can be seen that the adsorption rate of Cd(II) ions increased with the increase in pH, and consequently, the optimal pH was set at pH 5.0, in the sense that Cd(II) ions were quantitively adsorbed and not to deposit at pH 5.0. The results also showed the possibility of concentrating the metal cations working at a constant pH, which made sodium trititanate whisker a very promising sorbent.

![Figure 2. Effect of pH on the adsorption rate](image)

**B. Influence of the mass of sorbent**

In order to get the acceptable mass of sodium trititanate whisker for the adsorption of Cd(II) ions, the experiment was carried out at pH 5.0 according to the proposed method. The results were shown in Fig.3. Sodium trititanate whisker was used as sorbent; When its dosage was less than 0.10 g, the adsorption rate of Cd(II) ions was limited for its shortage; when its dosage was over 0.10 g, its adsorption rate can be over 92.3%. Taking one thing with another, the optimum mass of sorbent was 0.25 g.

![Figure 3. Effect of dosage of sorbent on adsorption rate](image)

### D. Effect of heater temperature on recovery

The influence of heater temperatures on recovery of Cd(II) was taken into account. The results are given as follows: Cd(II) ions were hard to be eluted at the room temperature, due to the positive effect of the temperature, moreover, the recovery had reached 100.3% at 100°C, and thus 100°C was chosen for subsequent procedure.

### E. Influence of eluent on recovery

As is shown from Fig.2 that the adsorption of Cd(II) ions at PH<5.0 was not ideal. So various concentrations of HCl were studied for desorption of adsorbed ions. The results obtained indicated that 2.0 mol/L of HCl was sufficient for complete elution at 100°C. In the light of the proposed experimental technique, the influence of different volumes of 2.0 mol/L of HCl on the recovery of Cd(II) ions was inspected. The results indicated that the increase on its level conferred improvement in analytical responses. Consequently, 10 mL of 2.0 mol/L of HCl solution was selected for the further experiments.

### F. Adsorption isotherm

The above results were carried out using relatively low concentrations of Cd(II) ions. In order to obtain information about the coverage of Cd(II) ions taken up on sodium trititanate whisker, and the equilibrium process, adsorption isotherms were obtained. Fig.4 indicates adsorption isotherm obtained at PH 5.0. It is evident that the mass added is different, but the irreversible and reversible adsorption regions are distinguished in all instances. This means that the analytes added are strongly adsorbed until the saturation of a definite part of the surface (i.e. the most active site). After filling of these sites, reversible adsorption of a Langmuir type occurs. In this part of isotherm, the amount adsorbed increases with
increase in concentration. However, ions adsorbed in this way are easily desorbed, and when the analyte concentration reaches zero (e.g. on washing), only the irreversibly adsorbed ions remain on the surface. Consequently, the first part of the adsorption isotherms is of definite interest for analytical applications. After the distribution equilibrium has been reached, the concentration of the metal ions in solution was determined by FAAS, and thus the static adsorption capacity of Cd(II) ions was obtained. Besides, Qs was 36.07 mg/g.

Figure 4. The adsorption isotherm (pH 5.0) of Cd(II) on sodium trititanate whisker

G. The adsorptivity of sodium trititanate whisker for some other ions

Under selected conditions, some experiments were carried out to examine the adsorption rate of sodium trititanate whisker for the following common ions: K(I), Na(I), Mg(II), Ca(II), Fe(III), Al(III), Mn(II), Co(II), Cr(III), Cu(II), Pb(II), Mo(VI). From the results obtained, it can be concluded that Ca(II), Co(II), Cr(III), Cu(II), Pb(II) ions can be quantitatively adsorbed on sodium trititanate whisker, and the adsorption rate of the other ions were much lower. The presence of major foreign metal ions has no important influence on the adsorption of ions under optimal conditions.

H. Detection limit and precision

The detection limit (3σ) of this method for Cd(II) is 0.015 mg/L; and the relative standard deviation is 1.31% for 1.0 mg/L Cd(II) ions (n=11).

IV. APPLICATION OF THE METHOD

2500 mL of water samples were acidified by 2.5 mL of HCl (1:1), respectively, then vaporized near 200 mL, cooled, and filtrated, the filtrates were diluted to 250 mL with distilled water.

The proposed method has been applied to the determination of Cd(II) in natural water samples by FAAS. The standard addition method was used, and the analytical results and the recovery were given in Table 1, the results indicated that the recoveries were reasonable for trace analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average value µg/mL</th>
<th>Added µg/mL</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td>0.024</td>
<td>0.2</td>
<td>96.50</td>
</tr>
<tr>
<td>Yudai River water</td>
<td>0.016</td>
<td>0.2</td>
<td>98.00</td>
</tr>
</tbody>
</table>

V. CONCLUSIONS

In this paper was shown the analytical performance of sodium trititanate whisker for on-line cadmium enrichment/separation. Cd(II) ions were quantitatively adsorbed at pH 5.0, and quantitatively eluted at 100 °C. Besides, Qs was 36.07 mg/g. In a word, these features indicate that sodium trititanate whisker due to its high ratio surface area and exchangeability with ions was an ideal sorbent.

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