



Simple and rapid spectrophotometric determination of trace titanium (IV) enriched by nanometer size zirconium dioxide in natural water

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ABSTRACT

A novel method for preconcentration of Ti(IV) with nanometer size ZrO₂ and determination by spectrophotometry has been developed. Ti(IV) was selectively adsorbed on 300 mg ZrO₂ from 500 mL solution at pH 6.0, then eluted by 5 mL 11.3 mol L⁻¹ HF. The eluent added was diantipyrylmethane (DAPM, as chromogenic reagent) and ascorbic acid (as masking agent), used for the analysis of Ti(IV) by measuring the absorbance at 390 nm with spectrophotometry, based on the chromogenic reaction between the Ti(IV) and DAPM. This method gave a concentration enhancement of 100 for 500 mL sample, eliminated the sizable interferences on direct determination with spectrophotometry. Detection limit (3σ, n = 11) of 0.1 μg L⁻¹ was obtained. The method was applied to determine the concentration of Ti(IV) in river water and seawater and the analytical recoveries of Ti(IV) added to samples were 97.6–101.3%.

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1. Introduction

A considerably high amount of titanium is released to natural water at the level of μg L⁻¹ [1,2] from stainless steel modification, light alloys, paper and pulp industry [3]. The maximum permissible concentration in water for titanium is 0.1 mg L⁻¹ [4]. Titanium overload can cause element imbalance which could induce many diseases [4].

Spectrophotometric methods offer the best alternative for routine analysis of titanium in the absence of ICP-AAS [5], ICP-AES [5], ICP-OES [6,7], and ICP-MS [8,9], owing to its rapidity and high selectivity [10]. Diantipyrylmethane (DAPM) as chromogenic agent is widely used for routine analysis of titanium [11], for its sensitivity (the apparent molar absorptivity 1.5 × 10⁴–1.8 × 10⁴) and a good stability of the yellow coloured complex from Ti(IV) and DAPM. The sensitivity of spectrophotometric methods is low for the determination of traces of titanium in natural water. Therefore, attempts have been made to enhance the sensitivity by combination with preconcentration methods including solvent extraction [12] and solid-phase extraction on supports as column [13], membrane filter [14], ion-exchange resin [15], naphthalene [13], and anionic iron chelate on chitin [21]. The concentration of the analyte can be increased

and most of the accompanying elements present in the matrix are not retained [17–19]. Using foregoing pretreatment methods, the enrichment factors are still undesirable for the low adsorption capability of the adsorbents. Nanometer materials can adsorb selectively metal ions, and have a very high adsorption capacity [20–22].

Zirconia (ZrO₂) has strong Lewis acid sites. The ZrO₂ preconcentration column has been used for selective preconcentration of chemical warfare agent degradation products [23], but the application of nanometer size ZrO₂ on the preconcentration of trace metals has not been reported until now. Usually titanium in environmental water mostly existed as tetravalent metal anions [24]. As a rule, on amphoteric oxide ZrO₂, anions were adsorbed when the pH value of the solution was below the point of zero charge (pH_{PZC}), whereas cations are adsorbed when the pH value was above the pH_{PZC}. Different ions, including cations and anions, have different electric quantity and quality, hydrated ionic radius, and binding energy with the adsorbent. The adsorbed ions are often very strongly held and elution could be achieved by dissolving the adsorbent. So far, ZrO₂ is used as an inorganic ion-exchange materials and selective adsorption and preconcentration of titanium, elimination matrix interferences might be achieved, controlling the pH value.

The aim of this work was to develop a valid routine method for the preconcentration of Ti(IV) based on quantitative adsorption on ZrO₂ with high surface areas, for elimination of the interferences based on the selective adsorption, for determination with spectrophotometric methods.

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2. Experimental

2.1. Apparatus

A UV-1200 PC spectrophotometer (Pekin Ruili Co., China) connected to a Legend Pentium IV computer was used for all the measurements and treatment of data. The pH was controlled with a model 320-S pH meter (Mettler Toledo Co., China) supplied with a combined electrode. A model JJ23DJ-1 magnetic stirrer (Shanghai Hexin Co., China), a model TD4 centrifugal machine (Hunan Centrifugal Machine Co., China) and Milli-Q water system (Millipore Co., Bedford, MA) were used for the test. PTFE laboratory vessels were used throughout.

2.2. Reagents

All chemicals were of trace metal grade levels and were provided by Merck (Darmstadt, Germany). All the solutions were made up by Milli-Q-purified water. Milli-Q-purified water, prepared by further purification of de-ionized water with a Milli-Q system was used. Working Ti(IV) solutions were made daily by appropriate dilutions of the stock Ti(IV) solution ($1000 \pm 2 \text{ mg L}^{-1}$ in 5 mol L^{-1} HCl) and appropriate amounts of HCl solution were added in order that all the resulted solutions have a final amount concentration of 0.06 mol L^{-1} . The addition of the HCl solution both prevented the hydrolysis of the Ti(IV) solutions and the standard solutions had the acidity that the real samples had after their pretreatment. DAPM solution containing 30 g L^{-1} was prepared freshly right before use by dissolving 3 g DAPM in 30 mL of 1 mol L^{-1} sulphuric acid and diluting to 100 mL with water. The standard solution of ascorbic acid (10 g L^{-1}) was prepared daily by dissolving 1 g of solid ascorbic acid in 100 mL water. Nanometer ZrO_2 was prepared as reference [25], XRD analysis showed it to be a spherical structure, and TEM revealed typical particle size of 30–40 nm.

2.3. Preparation of the samples

Water samples were filtered through a membrane of $0.45 \mu\text{m}$ to exclude insoluble particles. The filtrates from water samples were used for the further procedure of the preconcentration and the determination of titanium.

2.4. Procedure

Adjusting pH to 6.0, a sample solution of 500 mL was added to polyethylene beaker containing 300 mg ZrO_2 , stirred for 15 min for selective adsorption of Ti(IV), and centrifuged. The residue in centrifugal tube was washed twice with Milli-Q-purified water and 5 mL 11.3 mol L^{-1} HF solution was added to dissolve the adsorbed Ti(IV). When the residue was completely dissolved, the eluent 4 mL DAPM solution (as chromogenic agent) and 1 mL ascorbic acid solution (as masking agent) was added, stirred for 30 min, then used for the determination of Ti(IV) by spectrophotometry [26]. The absorbance on 390 nm was recorded with 1 cm quartz cell with reagent blank.

3. Results and discussion

3.1. Absorption wavelength

Both chromogenic agent and masking agent were added into a series of 4 mL standard solutions, containing 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, $0.5 \mu\text{g mL}^{-1}$ Ti(IV) respectively. To study the appropriate absorption wavelength, these solutions were stirred for 30 min, and then were used for the measure of the absorption spectra in the range of 330–800 nm. The maximum of absorbance and the

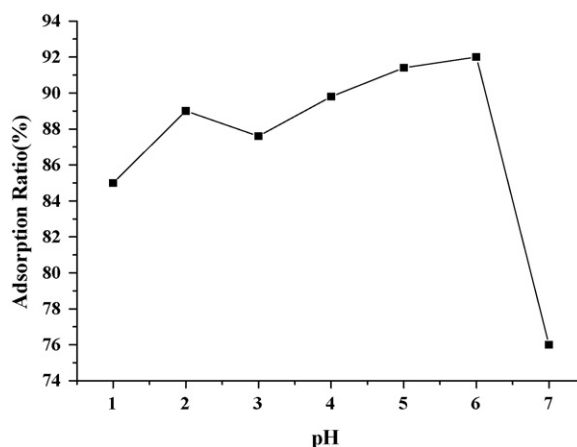


Fig. 1. Effect of pH on the adsorption of Ti(IV) (500 mL , $2.5 \mu\text{g mL}^{-1}$) on ZrO_2 (500 mg).

linear regression coefficients of the calibration graphs, r^2 , 0.999, were gained at 390 nm. So 390 nm could be used as an appropriate absorption wavelength.

3.2. Effect of pH on the preconcentration of Ti(IV)

The influence of pH on the adsorption of Ti(IV) by 500 mg ZrO_2 was studied in the range of 1.0–7.0. A series of 500 mL standard solutions containing $2.5 \mu\text{g mL}^{-1}$ Ti(IV) (i.e., $1250 \mu\text{g Ti(IV)}$) was added to polyethylene beaker, stirred for 30 min to adsorb Ti(IV), then centrifuged. The centrifugal liquid 2 mL was used for determining the concentration of Ti(IV) by a spectrophotometric method. The adsorption mass of Ti(IV) on the adsorbent was the product of sample volume (500 mL) and the concentration difference between initial sample solution and the centrifugal liquid. The adsorption ratio was the mass ratio between the adsorption mass of Ti(IV) on the adsorbent and $1250 \mu\text{g}$. Fig. 1 indicates the pH value played a determining role with respect to the adsorption of Ti(IV) on ZrO_2 . The best adsorption ratio was achieved at a pH value of 6.0 and this value was selected for the subsequent experiments.

Just as W(VI), the pH value of the solution greatly affected the polymerization process of Ti(IV) [21]. On different pH value, the species of Ti(IV) was different, its electric quantity, hydrated ionic radius, binding energy with the adsorbent and so on were also different. At the same time, the physical and chemical property of the nanometer adsorbent, such as surface composition, surface potential, surface energy, the quantity and quality of surface charge, could be changed with the change of the pH value. The surface charge of ZrO_2 particles was positive (or negative) when the pH values were below (or above) the pH of the point of zero charge ($\text{pH}_{\text{PZC}} = 6.6$) [27]. Because Ti(IV) existed as an anion, the greatest decrease of the adsorption ratio of Ti(IV) occurred when the pH value of the solution was changed from 6.0 to 7.0 for the change of the surface charge of ZrO_2 particles.

3.3. Effect of the dose of nano- ZrO_2 on the adsorption ratio to Ti(IV)

Adjusted pH to 6.0, 500 mL of $2.5 \mu\text{g mL}^{-1}$ standard solution of Ti(IV) was respectively added to 100, 200, 300, 400, 500, 700, 900 mg ZrO_2 (i.e., the dose of ZrO_2 was respectively 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.8 mg mL^{-1}), stirred for 30 min, and filtered. The residual titanium concentration was determined in the filtrate, then the adsorption ratio was calculated. Results were shown in Fig. 2.

The adsorption ratio was increased with the increasing of the dose of ZrO_2 from 0.2 to 0.6 mg mL^{-1} . When the dose was more

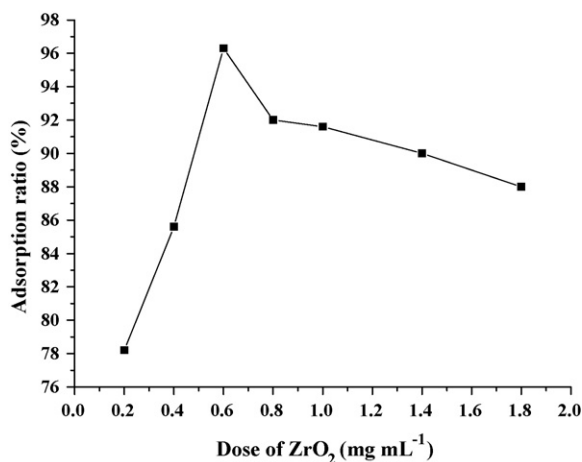


Fig. 2. Effect of the dose of ZrO₂ on the adsorption of Ti(IV) (500 mL, 2.5 μg mL⁻¹, pH 6.0).

than 0.6 mg mL⁻¹, the surface area of ZrO₂ might be decreased for its aggregation. The optimum dose of ZrO₂ was 0.6 mg mL⁻¹, at which the adsorption ratio was 96.3%. This optimum dose of ZrO₂ was used for the subsequent experiments.

3.4. Adsorption equilibration time of ZrO₂ to Ti(IV)

Because rapid adsorption was of great importance in analytical application, the study of the adsorption equilibration time was performed. The 500 mL solutions containing 300 mg ZrO₂ and 2.5 μg mL⁻¹ Ti(IV) were stirred from 5 to 30 min, centrifuged, and then the content of Ti(IV) in the centrifugal liquid was determined. The adsorption ratio in different adsorptive time was calculated and the adsorption equilibration time of 15 min for Ti(IV) was deduced from Fig. 3.

3.5. Adsorption capacity of ZrO₂ to Ti(IV)

The adsorption capacity was the maximum metal quantity taken up by 1 mg of adsorbent and given by μg metal mg⁻¹ adsorbent. The adsorption isotherm was defined as the plot of the adsorbed amount on ZrO₂ against the free concentration of Ti(IV) in an aqueous solution. The test solutions 500 mL containing 1.0, 2.0, 4.0, 5.0, 6.0, 7.0, 8.0 μg mL⁻¹ of Ti(IV), respectively, was added ZrO₂ 300 mg, stirred for 15 min, and centrifuged. The content in the centrifugate,

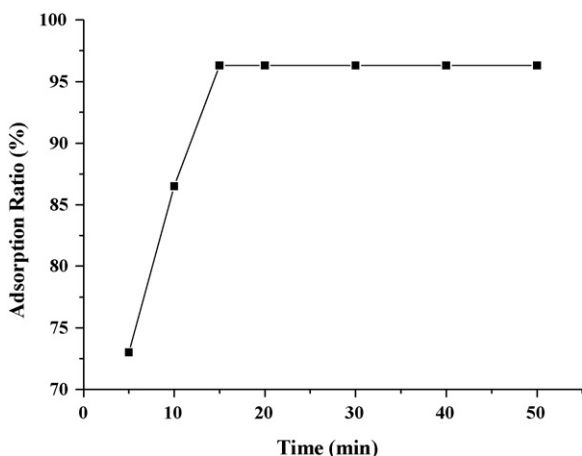


Fig. 3. Effect of the adsorption time on the adsorption of Ti(IV) (500 mL, 2.5 μg mL⁻¹, pH 6.0) on ZrO₂ (300 mg).

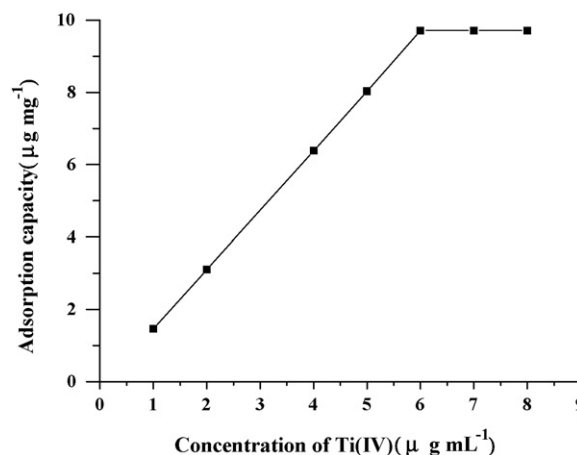


Fig. 4. Effect of the concentration of Ti(IV) (500 mL, pH 6.0) on the adsorption capacity of ZrO₂ (300 mg).

i.e., the free concentration of Ti(IV) after reaching the adsorption equilibrium, was determined, and then the adsorption isotherm of Ti(IV) could be constructed, shown on Fig. 4. The saturated adsorptive capacity of ZrO₂ was estimated at 9.71 μg mg⁻¹, more than that of ion-exchange resin [15] and anionic tiron chelate on chitin [16]. Two regions might be distinguished in the adsorption isotherm: irreversible and reversible adsorption. This meant that Ti(IV) added was strongly adsorbed until the saturation of a definite part of the surface (i.e., the most active sites). After filling of these sites, reversible adsorption of a Langmuir type occurred. In this part of the isotherm, the amount adsorbed was increased with the increase of the concentration of the analyte. However, ions adsorbed in this way were easily desorbed, and when the analyte concentration reached zero (e.g., on washing) only the irreversibly adsorbed ions remained on the surface [28]. Hence the first part of the adsorption isotherms was of a definite interest for analytical applications.

3.6. Effect of preconcentration factor on Ti(IV) adsorption

50-mg aliquot of ZrO₂ was added to (a) 500 mL solution containing 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 7.0, and 8.0 μg mL⁻¹ of Ti(IV), respectively, and (b) ZrO₂ (0.6 mg mL⁻¹) were then added to 6.0 μg mL⁻¹ Ti(IV) solutions of which volume increased from 50 to 500 mL. Then the adsorption ratio of Ti(IV) was calculated, and the results are shown in Tables 1 and 2.

Based on the results of experiments (a) and (b), one can conclude that the adsorption ratio of Ti(IV) was rested on both the pH value and the total amount of titanium in the solution. When the total amount of titanium was no more than 2.85 mg, i.e., the adsorptive capacity of ZrO₂ was less than 9.5 μg mg⁻¹, the adsorption ratio

Table 1

Dependence of adsorption ratio (%) of Ti(IV) on sample concentration (sample volume 500 mL).

	Concentration of Ti(IV) (μg mL ⁻¹)						
	1	2	4	5	6	7	8
Adsorption ratio (%)	97.3	96.9	96.7	96.4	95.5	83.1	72.9

Table 2

Dependence of adsorption ratio (%) of Ti(IV) on sample volumes (concentration of Ti(IV) 6.0 μg mL⁻¹).

	Sample volume (mL)				
	100	150	250	500	600
Adsorption ratio (%)	96.1	96.4	95.7	95.2	94.3

Table 3Elution data (%) for Ti(IV) adsorbed on ZrO₂ with different eluents.

	Eluent						
	Hydrochloric acid			Hydrofluoric acid			
Concentration (mol L ⁻¹)	2	3	4	6	8	8.0	11.3
Elution data (%)	70.1	70.6	80.4	85.1	92.1	87.7	98.2

of Ti(IV) could be higher than 95%, the constant and quantitative recovery of Ti(IV) could be obtained, and the adsorption ratio was enough for the preconcentration of Ti(IV) in samples.

3.7. Elution

Ti(IV) adsorbed on ZrO₂ from 500 mL solution containing 3 μg L⁻¹ Ti(IV), was washed twice with Milli-Q-purified, then eluted with 5 mL HCl or HF solution as the eluent. Table 3 presents the elution data (%) for Ti(IV) with different kinds and concentration of the eluent. As could be seen, 5 mL of 11.3 mol L⁻¹ HF solution was an appropriate eluent for the determination of titanium by the spectrophotometry with 4 mL DAPM solution (as chromogenic agent) and 1 mL ascorbic acid solution (as masking agent), because (a) the condition constant K_{Ti-F} of [TiF₆]²⁻ in 1.13 mol L⁻¹ HF media (log K_{Ti-F} = 11.57 ± 0.02) was high [29], so titanium could be eluted as [TiF₆]²⁻ by HF solution, and its elution data was 98.2%, (b) ZrO₂ could be dissolved by HF solution, becoming as [ZrF₆]²⁻, (c) the condition constant of titanium and DAPM was higher than K_{Ti-F} , fluoride ion as the ligand of titanium could be replaced by DAPM, and (d) the determination could not be interfered by the coexistence of high concentrations of zirconium [30] and fluoride [31].

3.8. Evaluation of interference

The effect of the major constituents of natural waters, especially the metal ions, on the preconcentration and determination of Ti(IV) by spectrophotometric method was investigated. The concentrations of foreign ions were chosen to be close or higher to their contents in natural waters. The matrix concentrations were varied, whereas the concentration of Ti(IV) was kept at 3 μg L⁻¹. The results indicated that no interference were observed when Ca²⁺ (160 mg), Mg²⁺ (400 mg), Cu²⁺ (10 mg), Fe²⁺ (10 mg), Fe³⁺ (5 mg), Al³⁺ (10 mg), Pb²⁺ (10 mg), Ni²⁺ (10 mg), Co²⁺ (10 mg), Mo²⁺ (10 mg), Zn²⁺ (10 mg), Mn²⁺ (10 mg), Ag⁺ (10 mg), Sb³⁺ (10 mg), Sn²⁺ (10 mg), Bi³⁺ (10 mg), Hg²⁺ (10 mg), Cr³⁺ (20 mg), CrO₄²⁻ (50 mg), VO₄³⁻ (20 mg), HCO₃⁻ (1000 mg), HPO₄²⁻ (500 mg), SO₄²⁻ (1000 mg) and Cl⁻ (2000 mg) were added to 500 mL solution.

The result suggested that the methods could be effectively used to quantitatively determine trace titanium in natural water. Because titanium and zirconium belong to IVB in the periodic table of elements, their resemblance in chemical nature results in their high mutual affinity, so Ti(IV) could be selectively adsorbed by ZrO₂.

3.9. Method performance

According to the above-mentioned procedure, a series of 500 mL of solutions containing 1 μg L⁻¹ Ti(IV) were measured. Detection limit (based on 3σ of the blank determinations, $n = 11$) of 0.1 μg L⁻¹ Ti(IV) and relative standard deviation of 3.1% were obtained. To study the accuracy of the method, a water certified reference material (CRM, GSB07-1977-2005, produced by China National Environmental Monitoring Centre) with total titanium content of 10.00 ± 0.40 μg L⁻¹, was analyzed. The content obtained in CRM was 10.00 ± 0.31 μg L⁻¹ for titanium. The result demonstrated that (a) the total content value obtained in CRM agreed well with the certified value and (b) this method gave a concentration enhance-

Table 4Analytical results of Ti(IV) in samples (μg L⁻¹).

Samples	Ti(IV) added	Ti(IV) found	Recovery (%)
Jiu-long river water	0.00	9.70 ± 0.04	–
	10.00	19.68 ± 0.03	99.8 ± 0.3
Zhang-pu seawater	0.00	5.27 ± 0.05	–
	5.00	10.19 ± 0.04	98.4 ± 0.8
CRM	0.00	10.00 ± 0.31	–
	10.00	20.07 ± 0.06	100.7 ± 0.6

ment of 100 for 500 mL sample volume, while obtaining low enough detection limits for Ti(IV) in natural water samples.

3.10. Analysis of real samples

The content of Ti(IV) in water samples collected at sites in Fujian Province, Zhangzhou City, China was determined by the proposed procedure. Analytical results of water samples were listed in Table 4.

The precision and accuracy of the method were tested by spiking the samples. The results showed that (a) the recoveries were reasonable for trace analysis, in a range of 97.6–101.3% and (b) total titanium in a CRM was also credible. No systematic error could be seen in the added–found method for titanium determination in water samples. The efficiency of the preconcentration and detection system was high.

4. Conclusions

This method was suitable for the preconcentration and direct determination of titanium in natural water, based on its high adsorbability, high concentration factor, and low detection limit. The features of this new technique are its low instrument and running costs, easy operation, and high sensitivity.

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