

Notes

Simple and Rapid Spectrophotometric Determination of Trace Titanium(IV) with Preconcentration as Its Anionic Tiron Chelate on Chitin

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The spectrophotometric methods for the determination of microamounts of titanium have been based on the complexes with hydrogen peroxide¹, 1,2-dihydroxybenzene-3,5-disulfonate (tiron)^{2,3}, chromotropic acid^{4,5} and diantipyrylmethane.^{6,7} These methods have comparatively high selectivity but low sensitivity. Therefore, attempts have been made to enhance the sensitivity by combination with preconcentration methods for the determination of traces of titanium, including solvent extraction⁸⁻¹¹ and solid-phase extraction on supports such as membrane filter^{12,13}, ion-exchange resin¹⁴ and naphthalene.¹⁵

The spectrophotometric, atomic absorption spectrometric and electroanalytical methods for many inorganic ions have been developed by using the collection process on chitin after their ions are converted into each suitable species such as colored metal complexes or anionic species.¹⁶⁻³⁰ Chitin, which is a natural amino polysaccharide and a hydrophilic polymer similar to cellulose, but is stable over a wide pH range of aqueous solution, has the excellent properties as the support for solid-phase extraction: namely, the collection and elution of species is rapid¹⁶⁻¹⁹, and its protonated acetyl amino groups act as anion-exchangers for various type of anionic species in weak acidic medium.²⁰⁻²⁹

In this paper we report on the spectrophotometric determination of trace amounts of titanium(IV) following the preconcentration procedures as follows: first the collection as its anionic tiron chelate on protonated chitin, and second the elution with a small volume of ammonia buffer solution. The proposed method was applied to the determination of titanium in environmental samples.

Experimental

Reagents and apparatus

A commercially available chitin powder (Funakoshi

Co., Ltd.) was washed successively with a 1 mol dm⁻³ hydrochloric acid solution, distilled water and methanol; it was then kept at 40°C for 24 h in a vacuum dry oven.

The standard titanium(IV) solution (Wako Pure Chemicals) was 1000 µg cm⁻³, and was further diluted as required. Disodium tiron solution (5×10⁻² mol dm⁻³) was prepared by dissolving 1.571 g of Tiron (Dojindo Laboratories) in water and diluting to volume in a 100 cm³ volumetric flask. Other chemicals used were of analytical grade.

All absorbance measurements were made with a Shimadzu UV-2400 PC spectrophotometer. A Hitachi-Horiba Model F-7_{AD} pH meter was used for all pH measurements.

Standard procedure

To a 100 cm³ of solution containing up to 1 µg of titanium(IV), add 0.2 cm³ of 5×10⁻² mol dm⁻³ tiron solution and 0.1 cm³ of 1 mol dm⁻³ acetate buffer solution (pH 5.5). Then pass the solution through a chitin column (polyethylene column, 6 mm i.d.×60 mm long, 50 mg of chitin) fitted with a porous polyethylene disk with a 20-µm pore size at a flow-rate of 15 cm³ min⁻¹. Elute the titanium-tiron chelate from chitin with 1 cm³ of 0.1 mol dm⁻³ ammonia buffer solution (pH 9.5), and measure the absorbance of the eluent at 381 nm.

Results and Discussion

Overall capacity

The overall capacity for titanium-tiron chelate on protonated chitin at pH 5.5 was examined by batch equilibration of 50 mg of chitin with 100 cm³ of solution containing 5×10⁻⁵ mol dm⁻³ of the titanium chelate. The equilibration could be achieved by agitating for over 60 min. After filtration, the amounts collected on chitin for titanium-tiron chelate were decided by comparing the concentration of the solutions before and after

equilibration spectrophotometrically. Their overall calculated capacity was $22.17 \mu\text{mol g}^{-1}$ and it corresponded to $53.1 \mu\text{g}$ of titanium(IV) per 50 mg of chitin. The capacity is sufficient to collect $1 \mu\text{g}$ level of titanium(IV), though its capacity is less than that of common anion-exchange resin.

Absorption spectra

The titanium-tiron chelate had an absorption maximum at 381 nm in 0.1 mol dm^{-3} ammonia buffer solution as the eluent, where the absorption of reagent blank was very small. The absorbance of the titanium chelate in the eluent was constant for about 2 h after elution. All absorption measurements were therefore carried out at 381 nm in this study.

Collection and elution conditions

Figure 1 shows the effect of pH on the collection of the titanium chelate on chitin. The titanium chelate was quantitatively collected from aqueous solution over a pH range of 4.7 to 6.0. It is likely that the collection percentage for titanium(IV) on chitin decreases due to the insufficient complex formation with tiron down to pH 4.7 and due to the decrease in the amount of the effective protonated chitin beyond pH 6.0. In this study, the optimum pH of the solution on the collection was adjusted to be 5.5 by adding 1 mol dm^{-3} acetate buffer solution.

The effect of the reagent concentration on the collection was also examined. The quantitative collection was obtained in the concentration over a 60-fold molar excess of tiron to titanium(IV), when the sample solution contained $1 \mu\text{g}$ of titanium(IV). The reagent concentration was chosen as described in the standard procedure.

The effect of flow rate on the collection and elution was examined. The flow rate of sample solution on the collection was varied from 5 to $30 \text{ cm}^3 \text{ min}^{-1}$. The column was aspirated. The titanium chelate was quantitatively collected even when the flow rate was $30 \text{ cm}^3 \text{ min}^{-1}$.

Collection from 100 cm^3 solution containing $1 \mu\text{g}$ of titanium(IV) on a column with various amounts of chitin over the range of 20 to 60 mg was examined. The titanium chelate was quantitatively collected on a column containing up to 40 mg.

Recoveries of $1 \mu\text{g}$ of titanium(IV) from various volumes over the range of 100 to 500 cm^3 of sample solution were examined. The titanium chelate was quantitatively collected in this range. Thus, up to 500-fold concentration could be easily achieved.

The elution of the titanium chelate collected on a column of chitin was examined by using 0.1 mol dm^{-3} ammonia buffer solution over a pH range of 8 to 10 (Fig. 2). The elution of the titanium chelate was not quantitative with the ammonia buffer solution of pH 8 due to insufficient neutralization of the protonated chitin, while the titanium chelate was quantitatively eluted with the ammonia buffer solution of pH up to 8.5.

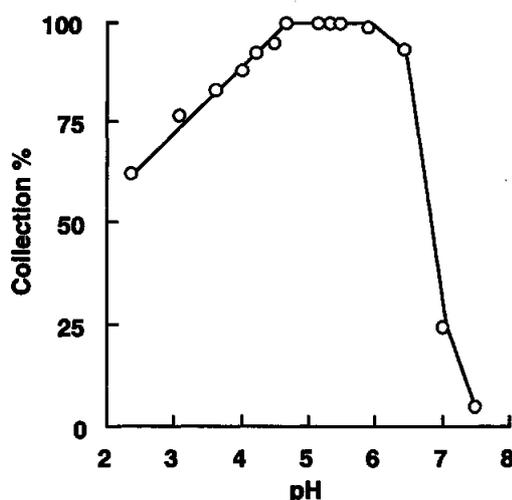


Fig. 1 Effect of pH on collection of titanium-tiron chelate. Conditions as in standard procedure except for pH of the sample solution.

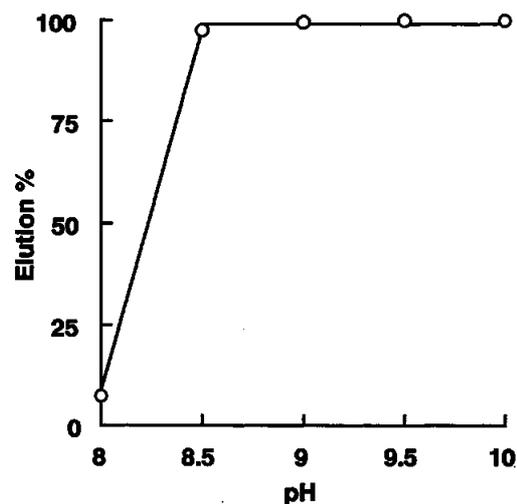


Fig. 2 Effect of pH of eluent on elution of titanium-tiron chelate from chitin. Eluent: 1 cm^3 of 0.1 mol dm^{-3} ammonia buffer solution. Conditions as in standard procedure except for pH of the eluent.

In this study, 0.1 mol dm^{-3} ammonia buffer solution of pH 9.5 was used as the eluent. The titanium chelate collected on the chitin was readily eluted with 1 cm^3 of the eluent within 1 min. Five successive collection and elution cycles with $1 \mu\text{g}$ of titanium(IV) on the same chitin gave almost identical results.

Calibration curve and precision

The calibration curve obtained by the standard procedure was linear over the concentration range of 0.1 to $1 \mu\text{g}$ of titanium(IV) in 1 cm^3 of the eluent. The apparent molar absorptivity was $12800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 381 nm. The relative standard deviation was 1.60% for

Table 1 Determination of titanium in standard samples

Sample	Sample taken/g	Ti found/ $\mu\text{g g}^{-1}$	Reported value/ $\mu\text{g g}^{-1}$
Pepperbush	0.0802	11.6	11 ^a
	0.0800	10.7	10.6 ^b
	0.0800	11.4	
		av. 11.2±0.5 RSD 4.5%	
Mussel	0.1000	8.6	6.4 ^a
	0.1000	7.6	8.2 ^b
	0.1005	7.8	
		av. 8.0±0.5 RSD 6.3%	
Chlorella	0.2002	5.2	3.1 ^a
	0.1999	5.2	2.4 ^b
	0.2000	4.6	
		av. 5.0±0.3 RSD 6.0%	

a. Ref. 14. b. Ref. 31.

0.5 μg of titanium(IV) (5 measurements).

Effect of diverse ions

The effect of diverse ions on the determination of titanium was examined. The tolerance limit was taken as being the amount causing an error $\pm 3\%$ in the absorbance of the eluent for titanium(IV) alone. For the determination of 1 μg of titanium(IV), Al^{3+} and Cu^{2+} in concentration up to 500 times, Hg^{2+} in concentration up to 100 times and Fe^{3+} in concentration up to 50 times that of titanium(IV) were tolerated when 10 mg of EDTA was added. CrO_4^{2-} in concentration up to 100 times, and MoO_4^{2-} and WO_4^{2-} in concentration up to 10 times that of titanium(IV) were tolerated when 10 mg of L-ascorbic acid and citric acid were added, respectively. The tolerance for limit for VO_3^- was low enough to give a positive error more than the equal amount of titanium(IV) due to the partial formation of its tiron chelate. Ca^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and AsO_4^{2-} did not interfere in concentrations up to 1000 times that of titanium(IV). Common inorganic anions such as F^- and Cl^- and organic acids such as citric acid, EDTA and L-ascorbic acid were tolerated in concentrations up to 10000 times that of titanium(IV).

Application

The presented method was applied to the determination of titanium in Pepperbush, Mussel and Chlorella issued by National Institute for Environmental Studies. Three replicate portions of each sample, after pre-treatment with concentrated nitric, perchloric and hydrofluoric acids, were analyzed by the standard procedure individually. The analytical results are shown in Table 1. The results for Pepperbush and Mussel show reasonable agreement with the reported values.^{14,31} The results for Chlorella, however, gave a

larger value than those reported probably due to the effect of iron containing a high ratio to titanium(IV) in the sample.

In conclusion, the collection of titanium-tiron chelate on chitin is affected by the pH of the solution. The elution of the titanium chelate from chitin is easily achieved with aqueous alkaline solution. These facts suggest that the anionic titanium chelate is largely collected by the electrostatic interaction between the anionic species and the surface of the protonated chitin. The presented method has the advantages of simplicity, rapidity and a high concentration factor.

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