

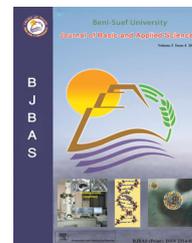
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Full Length Article

Preconcentration and determination of titanium in tap water, geological and sunscreen cream samples by CPE-FAAS method



Ardeshir Shokrollahi *, Masoud Gohari

Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran

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ABSTRACT

In the presented research, a cloud-point extraction method has been used for the preconcentration of trace amounts of Ti(IV) after complex formation with cupferron (phenyl-nitroso-hydroxylamine ammonium) using Triton X-114 as the surfactant. The chemical variables affecting the phase separation and the signal of flame atomic absorption spectrometry were optimized. At pH = 3.0, preconcentration of the analyte content sample in the presence of 0.07% (w/v) Triton X-114 and 8.6×10^{-5} M cupferron enabled the detection limit ($3S_b/m$) of 0.01 $\mu\text{g/mL}$ Ti(IV) and linear range 0.03–3.00 $\mu\text{g/mL}$ to be achieved. The enhancement factor and preconcentration factor were 37 and 30 respectively. The relative standard deviation by repeated assays of six separate solution of 0.67 $\mu\text{g/mL}$ Ti(IV) was also obtained 3.9%. The proposed method was applied to the determination of Ti(IV) in tap water, sand, feldspar, and sunscreen cream.

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1. Introduction

Titanium is the ninth most abundant element in the earth's crust and the fourth most abundant structural element. Titanium metal has become known as a space-age metal because of its high strength-to-weight ratio and inertness to many corrosive environments (Othmer, 1982). Alloys of this metal are also used principally in missile, aircraft parts and filament materials (in electrical applications) where lightweight, strength

and ability to withstand extremes of temperature are important. Besides its widespread industrial use, titanium has significant biological effects on plants, being beneficial at low, and toxic at higher concentrations (Kuzel et al., 2003). Titanium is an element which has an excellent biocompatibility and a high corrosion resistance. It has therefore become a widely used material for implants that can be fastened directly into human bone tissue (Rae, 1986). Therefore, it is important from the analytical point of view to develop simple, sensitive and reliable methods for the trace level

* Corresponding author. Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran. Fax: +98 74 33242147.

E-mail address: ashokrollahi@mail.yu.ac.ir (A. Shokrollahi).

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determination of titanium in various matrices in the presence of different ions.

Various analytical techniques have been used for the determination of titanium in different matrices including flame photometry (Chakrabarti et al., 1962), flame atomic absorption spectrometry (FAAS) (Grossmann, 1987) electrothermal atomic absorption spectrometry (ET-AAS) (López-García et al., 2004) inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Cardona and Meléndez, 2006), X ray fluorescence spectroscopy (XRF) (Melquiades et al., 2008), Spectrophotometry (Varghese et al., 2005), kinetic spectrophotometry (Zavvar Mousavia and Pourreza, 2008), spectrofluorimetry (Manuel-Vez and Garcia-Vargas, 1992) potentiometry (Khalifa et al., 1988), stripping voltammetry (Croot, 2011), and HPLC determination (Nagaosa and Segawa, 1994).

Due to analyte levels lower than the quantitation limits of instrumental techniques and interferences effects, separation and preconcentration technique such as liquid-liquid extraction (Mondal and Tarafder, 2004), ion-exchanger resin (Capitán-Vallvey et al., 1989), solid phase extraction (Aydin and Soylak, 2010; Shokrollahi et al., 2013b) and coprecipitation (Bakeeva et al., 2008; Shokrollahi and Gohari, 2014, in press) are used prior to titanium or other analytes determination.

The use of micellar systems have also been exploited in the different fields of analytical chemistry, mainly those focusing on the separation and preconcentration based on cloud-point procedures (Shokrollahi and Aghaei, 2014; Shokrollahi et al., 2011, 2013a).

Cloud-point extraction (CPE) is one of the most versatile and simple method for the preconcentration and extraction of hydrophobic species from water and environmental samples. The technique is based on the property of the most non-ionic surfactant in aqueous solutions which form micelles and become turbid when heated to a temperature known as the cloud-point temperature (CPT). Above the CPT, the solution is separated into two phases; a rich phase containing a high surfactant concentration in a small volume and a poor phase with a surfactant concentration close to the critical micelle concentration (CMC) (Stalikas, 2002). Hydrophobic species present in samples are able to interact with the micelles, thus being concentrated in the small volume of the surfactant-rich phase. Compared with traditional solvent extraction, CPE uses low toxic and environmental friendly surfactants rather than using of large amounts of toxic and flammable organic solvents. Cloud point extraction of titanium based on morin-titanium complex using Triton X-114 as the surfactant (Mirzaei and Karimi Naeini, 2013) and using Triton X-100 as the surfactant for determination of titanium in micellar medium with salicylaldehyde p-hydroxybenzoylhydrazone (SAPBH) complexing agent (Khadar and Varghese, 2005) have been reported recently.

Cupferron (Fig. 1), the ammonium salt of N-nitroso-N-phenylhydroxylamine, is a common reagent for the complexation of metal ions such as VO_3^- , Sn(II), Cu(II), Fe(III), Bi(III), Zr(IV), and Ti(IV) in acid media (Dean, 1999). The anion binds to metal cations through the two oxygen atoms, forming five-membered chelate rings.

In this work, cloud-point extraction has been used for the preconcentration and extraction of trace amounts of Ti(IV) after the complex formation with cupferron, using Triton X-114 as the surfactant and analysis by FAAS.

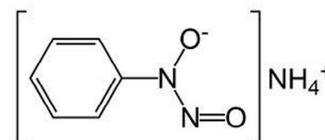


Fig. 1 – Structure of cupferron.

2. Experimental

2.1. Instrument

All determination was performed by using a Perkin-Elmer Atomic Absorption Spectrophotometer (Model 460) equipped with Ti Hollow cathode lamp and the nitrous oxide burner head. The lamp current was adjusted to 40 mA. The wavelength and slit were 364.3 and 0.2 nm respectively. The fuel to oxidant ratio was adjusted to form a reducing (rich-red) flame. The pH values of the solutions were measured by a Metrohm (Model 620) pH meter equipped with Metrohm combined glass electrode. A Sartorius (model TE214S) microbalance was used for weighing the chemicals. A Laboratory Centrifuge Machine (Model Y J 03-043-4000 China) was used to accelerate the phase separation process. The solutions temperature was thermostated at the desired temperature by a thermostat bath (model Huber CC305).

2.2. Reagent and solution

All chemicals used in this work, were of analytical-reagent grade. Double distilled water was used throughout. Analytical-grade methanol, ethylacetate, hydrochloric acids, and caustic soda were purchased from Merck, Darmstadt, Germany. A stock solution of Ti(IV) 1000 $\mu\text{g/mL}$ from Fluka, Buchs, Switzerland was used, and test solutions of Ti(IV) were prepared by diluting appropriate amounts of it in double distilled water. A Lithium metaborate from J.T. Baker® Chemicals was used as flux, for the real samples preparation. A 1.0% (w/v) Triton X-114 was prepared by dissolving 1.0 g of Triton X-114 from Fluka A. G., Buchs, Switzerland in 100 mL volumetric flask with stirring. A solution of 6.4×10^{-4} M cupferron was prepared by dissolving 0.0100 g cupferron (Merck) in double distilled water and diluted to 100 mL. Cupferron and the dilute Ti(IV) solutions were made fresh.

2.3. Procedure

For all optimization, a 15.0 mL centrifuge tube containing 0.67 $\mu\text{g/mL}$ of Ti(IV), 0.07% (w/v) of Triton X-114, and 8.6×10^{-5} M of cupferron adjusted to pH = 3.0 by addition appropriate values of NaOH 0.1 M. After several times shaking, the tube was left to stand in a thermo-stated bath at 60 °C for 10 min. The phase separation was achieved by centrifugation at 4000 rpm for 5 min. The tube was cooled in an ice bath for 5 min so that the surfactant rich phase would regain its viscosity. Afterward the bulk aqueous phase was easily decanted and the remaining micellar phase was dissolved in 60% ethylacetate + 40% methanol solvent to 0.50 mL. The titanium content of the prepared organic solution was readily determined by FAAS.

2.4. Preparation of real samples

The water samples were filtered through a Millipore cellulose membrane of pore 0.45 μm and were stored in polyethylene bottle. 10 mL of these samples were analyzed according to the procedure given in the section 2.3.

Geological samples (sand and feldspar) were prepared from fusing 0.1000 g of them with about 0.6 g of lithium metaborate in a platinum crucible at 1000 $^{\circ}\text{C}$ follow dissolving the melt with hot dilute HCl solution, transferring to a 250 mL polyethylene volumetric flask, and diluting to volume with double distilled water (Delijska et al., 1988). 10 mL of these samples were analyzed according to procedure given in the section 2.3.

Sunscreen sample was prepared from burning 0.1 g of it at 450 $^{\circ}\text{C}$ in a platinum crucible. After cooling, ash content was treated according to the procedure mentioned above for geological samples. 1 mL of prepared solution was analyzed according to procedure given in the section 2.3.

3. Result and discussion

The aim of this work is to develop a simple, sensitive and available method for the preconcentration and determination of trace amounts of Ti(IV) in various real samples using FAAS coupled with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and cupferron concentrations, heating time and temperature, centrifuge time and rate, as well as the effect of electrolyte on recovery of analyte, were investigated and optimized.

3.1. Effect of type of solvent

Cupferron-Ti(IV) complex in surfactant rich phase dissolve readily in ethylacetate. Since the surfactant rich phase contains a little water and ethylacetate are water insoluble, tolerable amounts of methanol added to ethylacetate to ensure water solubility of mix solvent. Acceptable recovery of Ti(IV) was found when mixture solvent (60% ethylacetate + 40% methanol) was applied for dissolution of surfactant-rich phase. Dillution of ethylacetate with methanol also decreased the viscosity of ethylacetate and facilitate atomic absorption aspiration.

3.2. Effect of pH

The formation of the metal-chelate and its chemical stability are the important factors influencing CPE. The pH plays a unique role in metal-chelate formation as well as extraction efficiency, proving to be the main parameter for CPE. Thus, a set of similar experiments in the pH range of 2.0-7.0 was conducted according to the procedure described in section 2.3. The results are illustrated in (Fig. 2). The maximum recovery was obtained at the pH = 3.0. In the pH < 3.0, recovery of analyte due to the protonation of ligand is low, while at the pH > 3.0, reducing of recovery is presumably due to precipitation of Ti(IV) ions in the form of hydroxides. Finally, pH = 3.0 was selected for the subsequent studies.

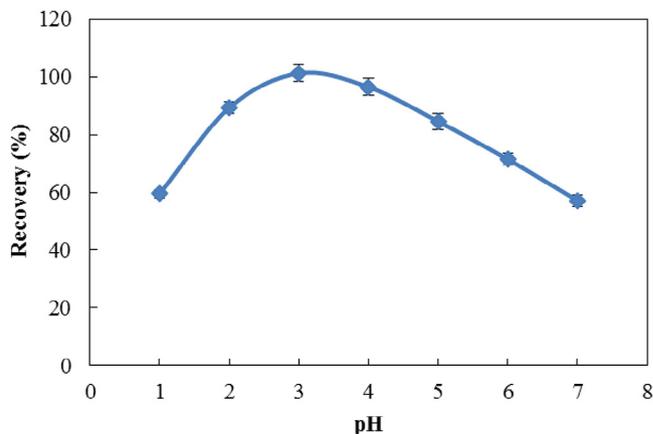


Fig. 2 – Effect of the pH on the recovery of analyte: 0.67 $\mu\text{g}/\text{mL}$ of Ti(IV), 0.07% (w/v) of Triton X-114, 8.6×10^{-5} M of cupferron, initial volume 15.0 mL, at 60 $^{\circ}\text{C}$.

3.3. Effect of cupferron concentration

The concentration of cupferron was investigated in the range of 1.0×10^{-5} – 1.1×10^{-4} M. For this study, 15.0 mL of a solution containing (0.67 $\mu\text{g}/\text{mL}$) of Ti(IV) ion and 0.07% (w/v) of Triton X-114 with various amounts of cupferron was applied to the cloud point preconcentration process. The recovery of analyte as a function of the cupferron concentration is shown in (Fig. 3). The FAAS signal increased up to a concentration of 8.6×10^{-5} M and reached to a near quantitative extraction efficiency, hence concentration of 8.6×10^{-5} M of cupferron was chosen for the subsequent experiments. In low concentration of cupferron, the extraction of titanium due to lack of cupferron concentration is not complete, whereas in higher concentration of ligand (8.6×10^{-5} M or over) the extraction output is satisfactory, therefore the concentration of 8.6×10^{-5} M of cupferron was selected for the CPE procedure.

3.4. Effect of Triton X-114 concentration

A successful cloud point extraction would be of that which maximizes the extraction efficiency through minimizing the

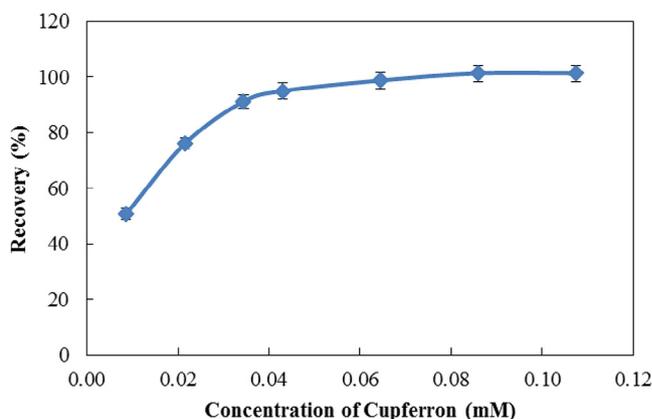


Fig. 3 – Effect of the cupferron concentration on the recovery of analyte: 0.67 $\mu\text{g}/\text{mL}$ of Ti(IV), 0.07% (w/v) of Triton X-114, pH = 3.0, initial volume 15.0 mL, at 60 $^{\circ}\text{C}$.

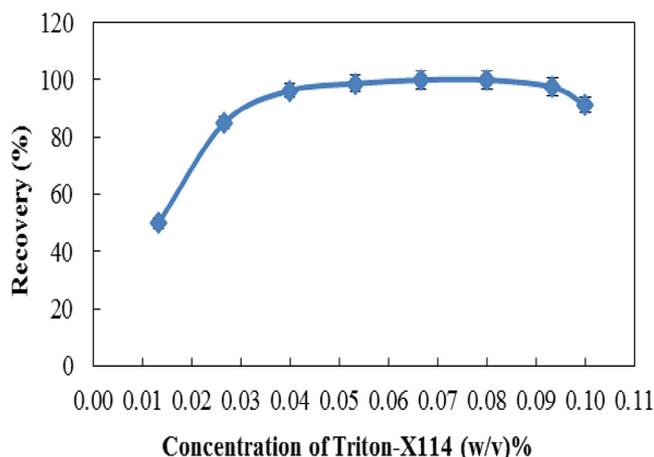


Fig. 4 – Effect of the Triton X-114 concentration on the recovery of analyte: 0.67 $\mu\text{g/mL}$ of Ti(IV), 8.6×10^{-5} M of cupferron, pH = 3.0, initial volume 15.0 mL, at 60 °C.

phase volume ratio. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud-point temperature and high density which facilitates the phase separation by centrifugation. The variation in the extraction efficiency versus the surfactant concentration was examined within the range of 0.01–0.10% (w/v). The results are shown in (Fig. 4). It was proved that Triton X-114, effectively extracts Ti(IV) complex from aqueous samples at a concentration of 0.07% (w/v). With an increase of the Triton X-114 concentration above 0.09%, the recovery of analyte due to viscosity increment of the surfactant rich phase (which is not favored in FAAS) decreased. Optimum surfactant concentration of 0.07% (w/v) was selected for Ti–cupferron complex to achieve the optimal analytical signal in conjunction with the highest possible extraction efficiency.

3.5. Effect of temperature and equilibrium time

It was desirable to employ the shortest equilibrium time with the lowest possible equilibrium temperature as a compromise between completion of extraction and separation of the phases. The dependence of extraction efficiency upon equilibrium temperature and time (above the cloud point) in the range of 30–80 °C and 5–30 min were thoroughly optimized. Holding the sample solutions for 10 min at 60 °C was found to be satisfactory to achieve acceptable micelle formation, quantitative extraction, and experimental convenience.

3.6. Effect of centrifuge time and rate

Short time without sacrificing extraction efficiency is also desirable for a preconcentration method. The centrifuge time and rate of centrifuge are two effective parameters in the time of cloud point experiments. Therefore, CPE on a set of experiments using 15.0 mL samples under optimum conditions by heating to 60 °C and centrifuging at various rates and times was carried out. Centrifugation at 4000 rpm for 5 min sufficed complete phase separation. The enrichment phase was

Table 1 – Effect of diverse ions on the Ti(IV) recovery: 0.67 $\mu\text{g/mL}$ Ti(IV) in optimum condition.

Ion	Concentration ($\mu\text{g/mL}$)
NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , B^{3+} (as H_3BO_3), Si(IV) (dissolved SiO_2), Cl^- , NO_3^- , Br^- , I^- , SO_4^{2-}	1000
Fe^{3+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , Cr^{3+} , Co^{2+} , Hg^{2+} , $\text{Cr}_2\text{O}_7^{2-}$	100
Mn^{2+} , Sn^{2+} , Bi^{3+} , F^- , PO_4^{3-}	10
Cu^{2+} , Zr(IV) , MoO_4^{2-} , VO_3^- (dissolved NH_4VO_3)	1

* Masked with ascorbic acid.

not separated completely at lower rates and centrifugation times.

3.7. Effect of the ionic strength

It is known that ionic strength of the solution is one of the effective factors in CPE. In this work, the effect of KCl salt as an electrolyte in the range of 0.01–0.50 M on the process was investigated. It was observed that increasing concentration of salt up to 0.2 M exerts no effect on the process but the higher concentrations create an adverse effect in recovery of the analyte. This effect might be explained by the additional surface charge which is created in the high ionic strength media.

3.8. Analytical performance

Calibration graph was obtained by preconcentration of 15.0 mL of solutions containing the various concentrations of Ti(IV) under optimum conditions. The linearity was observed in the range of 0.03–3.00 $\mu\text{g/mL}$. The equation of calibration graph was $y = 0.1113C + 0.007$ with correlation coefficient of 0.9986. The precision of the method was calculated by repeated assays of six same solution containing 0.67 $\mu\text{g/mL}$ Ti(IV). In this regard, the relative standard deviation was calculated as $\pm 3.9\%$. Since the equation of calibration curve of direct signal of AAS was $y = 0.0033C + 0.005$, the enhancement factor, which is the slope of calibration curve of coprecipitation procedure divided by slope of calibration curve of direct AAS was calculated as 37. Preconcentration factor which is the ratio of final volume (0.50 mL) over initial volume (15.0 mL) also was calculated as 30. The limit of detection ($3S_b/m$) was calculated as 0.01 $\mu\text{g/mL}$ which is sufficiently low in comparison of those attain by direct FAAS.

3.9. Interference studies

In order to assess the possible analytical applications of presented CPE procedure, the effect of some foreign ions that ordinarily exist in various real samples or react with cupferron was examined. The recovery of analyte was considered to be generally higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that cause an error not exceeding 5% in the determination of Ti(IV) by the CPE method. The results are given in Table 1. There was no significant interference of NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , B^{3+} (as H_3BO_3), Si(IV) (dissolved SiO_2), Cl^- , NO_3^- , Br^- , I^- , and SO_4^{2-} at 1000 μg

Table 2 – Ti(IV) determination in water sample (n = 4).

Sample	Added (µg/mL)	Found (µg/mL)	Recovery (%)
Tap water (Ahmad Abad, Shiraz, Iran)	0.00	ND*	–
	0.20	0.21 ± 0.01	105.0
	0.40	0.41 ± 0.01	102.5
	0.60	0.62 ± 0.02	103.3
	0.80	0.80 ± 0.02	100.0

* Not detected.

mL level; also no significant interference of Fe³⁺ (masked with ascorbic acid), Zn²⁺, Pb²⁺, Ni²⁺, Cr³⁺, Co²⁺, Hg²⁺, and Cr₂O₇²⁻ at 100 µg/mL level. Low tolerable level (10 µg/mL) for Mn²⁺, Sn²⁺, Bi³⁺, F⁻, and PO₄³⁻, and even less tolerable level (1 µg/mL) was found for Zr(IV), Cu²⁺, MoO₄²⁻ and VO₃⁻.

3.10. Application to real samples

In order to estimate the accuracy of the presented CPE procedure, 10 mL of water sample, 10 mL of the geological solution (sand and feldspar), and 1 mL of sunscreen solution, as prepared according to the procedure explained in section 2.4 were analyzed for Ti(IV) determination with the presented method separately. Different amounts of Ti(IV) standard solution were also spiked to the samples. The recovery values were generally higher than 95%. As shown in Tables 2 and 3, good agreement was obtained between the added and the measured analyte amounts, suggesting that the presented method is suitable for the same types of samples.

4. Conclusion

Although flame atomic absorption spectrometric (FAAS) method is an efficient analytical tool for determining trace amounts of titanium in different samples, high dissociation energy of titanium oxide (which forms in flame after aspiration of Ti(IV) content solution) and low molar absorbance coefficient of titanium are the reasons for increasing its detection limit.

Moreover many elements interfere with titanium absorption and cause difficulties in titanium determination. Therefore, FAAS determination of titanium is challenging and it is important from the analytical points of view to develop a simple, sensitive and reliable methods for the determination of trace amounts of titanium in different matrices. The proposed cloud point extraction procedure using cupferron, as a stable and fairly selective complexing agent, offers a simple, rapid, inexpensive and environmentally benign method for preconcentration and separation of titanium from aqueous solutions. The presented method has also a low limit of detection and good relative standard deviation which offers reliable results when applied for the determination trace amounts of titanium in the various real samples.

In this work, the ethylacetate-methanol mixture solvent was introduced for dissolving surfactant-rich phase instated of methanol as a routine solvent in most of CPE works. It is a good solvent for dissolution of Ti-Cupferron complex in enriched phase. It is notable that the ethylacetate is a good solvent for dissolving enriched phase, and methanol decreases the viscosity of it, for facilitating FAAS aspiration.

For comparison, merit numbers of the presented method have been compared with some previous methods of titanium determination. As shown in Table 4, the limit of detection of proposed method is less than spectrophotometry-CPE (Khadar and Varghese, 2005). Also the RSD of the presented method is better than electrothermal-AAS (López-García et al., 2004) and is similar to FAAS-CPE (Mirzaei and Karimi Naeini, 2013). The dynamic range of the proposed method is broader or equal to all reported methods in Table 4. In addition, this method has a good preconcentration factor in comprising to all reported methods in Table 4, except for FAAS-CPE (Mirzaei and Karimi Naeini, 2013).

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Table 3 – Ti(IV) determination in geological and sunscreen cream samples (n = 4).

Sample	Added (µg/mL)	Found (µg/mL)	Recovery (%)	Value in sample (µg/g)
Sand (quarry of Ardekan, yazd, Iran)	0.00	0.10 ± 0.01	–	246 ± 9
	0.20	0.30 ± 0.01	100.0	
	0.40	0.49 ± 0.02	97.5	
	0.60	0.70 ± 0.02	100.0	
	0.80	0.91 ± 0.03	101.3	
Feldspar (quarry of Mehdi-Abad, Hamedan, Iran)	0.00	0.39 ± 0.01	–	971 ± 35
	0.20	0.58 ± 0.02	95.0	
	0.40	0.79 ± 0.03	100.0	
	0.60	0.99 ± 0.03	100.0	
	0.80	1.20 ± 0.04	101.2	
Sunscreen cream (SPF60 Hydroderm, Iran)	0.00	0.50 ± 0.02	–	12,500 ± 490
	0.20	0.70 ± 0.03	100.0	
	0.40	0.89 ± 0.03	97.5	
	0.60	1.11 ± 0.04	101.7	
	0.80	1.29 ± 0.04	98.7	

Table 4 – Comparison of presented method for Titanium determination with some previous methods.

Method	LOD ($\mu\text{g/mL}$)	RSD (%)	Dynamic range ($\mu\text{g/mL}$)	Preconcentration factor	Reference
Electrothermal AAS	34 ^a	4.1	0–4500 ^b	1	López-García et al., 2004
Spectrofluorimetry	1.5×10^{-3}	0.8	0.005–0.05	1	Manuel-Vez and Garcia-Vargas, 1992
ICP-MS (SPE)	0.11×10^{-3}	3.2	0.08–0.2	20	Aydin and Soylak, 2010
FAAS-CPE	2.9×10^{-3}	3.8	0.02–2.0	61	Mirzaei and Karimi Naeini, 2013
Spectrophotometry (Micellar medium)	0.037	0.88	0.15–2.0	1	Khadar and Varghese, 2005
FAAS-CPE	0.01	3.9	0.03–3.0	30	This work

^a $\mu\text{g/g}$.
^b μg slurry.

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