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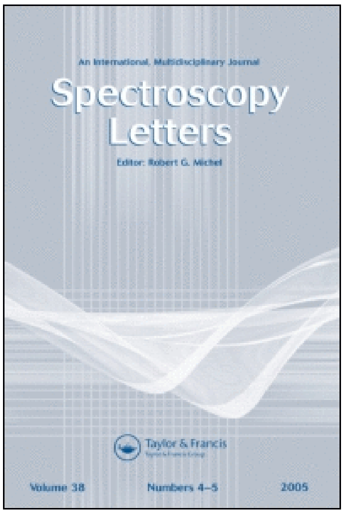

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 08 May 2004

To cite this Article Vojković, Vlasta , Živčić, Vlasta Allegretti and Drušković, Vinka(2004) 'Spectrophotometric Determination of Titanium(IV) by Extraction of its Thiocyanate Complex with Cationic Surfactants', Spectroscopy Letters, 37: 4, 401 — 420

To link to this Article: DOI: 10.1081/SL-120039590

URL: http://dx.doi.org/10.1081/SL-120039590

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SPECTROSCOPY LETTERS
Vol. 37, No. 4, pp. 401–420, 2004

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Spectrophotometric Determination of Titanium(IV) by Extraction of its Thiocyanate Complex with Cationic Surfactants

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ABSTRACT

A spectrophotometric method for the determination of titanium(IV) is described. It is based on the extraction of titanium(IV) as an ion-associated complex, formed between the titanium(IV)–thiocyanate anion and the cetyltrimethylammonium (CTMA), cetylpyridinium (CP), or tetradecyldimethylbenzylammonium (TDMA) cation in chloroform or dichloromethane. Optimum conditions for the extraction and spectrophotometric determination of titanium(IV) by all extractants were determined. The effect of chloride ions on the extraction was also examined. In their

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DOI: 10.1081/SL-120039590
0038-7010 (Print); 1532-2289 (Online)
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presence the systems studied were most sensitive. The apparent molar absorptivities of the complex, at 420 nm, and limit of detection, in the presence of chloride ions, were (6–7) × 10^4 L mol^{-1} cm^{-1} and 20–35 ng Ti(IV) mL^{-1}, respectively, depending upon the reagent used. Titanium determination was feasible in the presence of many foreign ions. The ratios of titanium(IV) and CTMA, CP or TDMA determined by Job's method were 1 : 2. The validity of the method was tested on bauxite and aluminum alloy samples. The values determined were in good agreement with the certified values.

Key Words: Titanium; Cationic surfactants; Extraction; Spectrophotometry; Aluminum alloy.

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INTRODUCTION

Commercially, the importance of titanium has been rapidly increasing. Titanium and its alloys find useful application in defence industry, particularly in manufacture of aircraft, missiles and in rocketry. Small amounts of titanium are present in glass, quartz, and pure zirconia and alumina. Its content in igneous rocks, which is usually lower than 2% m/m is relevant in elucidating the mode of rock formation. Titanium has been detected in seawater. Many plants such as grains, vegetables, trees, and shrubs contain titanium. Trace amounts of titanium are also found in all forms of animal life.[1] Therefore, the need for routine determination of titanium in such materials, as essential for their characterization, evaluation, and quality control, has been receiving increasing attention.

Many organic reagents for the extraction–separation and/or spectrophotometric determination of titanium have been reported. In search of a simple mode of spectrophotometric determination 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone has been used as chromogenic reagent.[2] The potential of 3,4-dihydroxybenzoic acid as a spectrophotometric reagent for titanium(IV) ions has been investigated by Ferreira et al.[3,4] An extractive spectrophotometric method for the determination of titanium(IV) has been developed using 2,3-dihydroxynaphthalene.[5] A spectrophotometric method based on the reaction of titanium(IV) with 6-(4-nitrophenylazo)-3,4,5-trihydroxy benzoic acid in ethanol medium has been successfully applied for its determination in soil and standard geological samples.[6] A method for the determination of titanium in aqueous medium by first-order derivative spectrophotometry using 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone has been reported by Babaiah et al.[7] Reactions between titanium(IV) or iron(III) and 2-(2-thiazolylazo)-*p*-cresol in aqueous methanol media have served for simultaneous spectrophotometric determination of titanium and iron in various standards and samples.[8] The existing methods, however, suffer from a number of drawbacks: low sensitivity,[2,3,5−7] coextraction of a large number of metal ions,[2,3,8] long extraction time,[5] critical pH.[6,7]

One of the commonest and most extensively used procedures for the spectrophotometric determination of titanium is the thiocyanate method. Titanium forms a yellow complex with thiocyanate ions in acidic media. The intensity of the "color" depends on the acid used, temperature, and even on the sequence in which the reagents are added.[9−11] The stability of the titanium–thiocyanate complex has been enhanced by the addition of a second ligand, e.g., tetraphenylarsonium chloride,[12] 1-phenyl-2-methyl-3-hydroxy-4-pyridone,[13] monooctyl-α-anilinobenzyl-phosphonate,[14] *N*-hydroxy-*N*,*N*′-diphenylbenzamidine,[15] which forms a mixed complex that is insoluble in water and is extractable into an organic solvent. A method for selective extraction of titanium–thiocyanate complex on polyurethane foam and its spectrophotometric determination in glass and ceramic materials have been described.[16]

Introduction of commercial extractants has increased the interest in the use of various surfactants as extractants in the hydrometallurgical metal processing. Since the last decade, surfactant reagents have extensively served for solvent extraction of various metal ions and are distinguished by a very good extractability and high separation efficiency.[17] Mixed-ligand complexes have been of increasing use, particularly in spectrophotometric analysis, because of their high sensitivity and selectivity.[18,19] The efficiency of extraction of the anionic titanium(IV)–thiocyanate complex from aqueous solutions with tricaprylmethylammonium chloride (Aliquat-336) in benzene has been investigated. The distribution coefficient was calculated from the concentration ratio of the titanium in the organic phase to the metal left in the water solution. The titanium(IV) concentrations in the organic phase (which were stripped) and in aqueous phase after extraction were determined by indirect EDTA titration.[20] However, the potential Aliquat-336 as a spectrophotometric reagent for titanium determination has not been explored.

In the present paper, a sensitive, selective, and reproducible extractive spectrophotometric method is described. It is based on the extraction of a mixed anionic titanium(IV)–thiocyanate–chloride complex from aqueous solutions by the cationic surfactants, cetyltrimethylammonium bromide (CTMAB), cetylpyridinium chloride (CPC), or tetradecyldimethylbenzylammonium chloride (TDMAC), and on its spectrophotometric determination in the organic phase. The method has been successfully applied for the determination of titanium in real samples.

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EXPERIMENTAL

Solutions or Reagents

A standard solution of titanium (0.01 M) was prepared by fusing 0.8 g of titanium dioxide (Riedel, Germany) with potassium hydrogen sulfate (Kemika, Croatia) in a platinum crucible. The cooled melt was extracted with dilute sulfuric acid (1 : 9), and the solution was filtered (B-4) and diluted with the same acid to 1 L. The solution was standardized by the cupferrone method.[21] To prevent the formation of hydrolyzed titanium species, more dilute solutions were always freshly prepared by appropriate dilution of the stock solution with deionized water.

Solutions of sodium or ammonium thiocyanate and lithium chloride were prepared by dissolving a weighed amount of dried analytical grade substances (Fluka, Switzerland) in deionized water. The hydrochloric and sulfuric acids of analytical reagent grade (Kemika, Croatia) were used to control the acidity of the solutions.

Cationic surfactant solutions were prepared by dissolving commercially manufactured CTMAB, CPC, or TDMAC (Fluka, Switzerland) in chloroform or dichloromethane, and diluted to 100 mL with organic solvent.

Chloroform and dichloromethane (Kemika, Croatia) of analytical reagent grade were used without further purification.

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Apparatus

A Varian double-beam spectrophotometer, Model Cary 3 (Australia), equipped with 1-cm quartz cells, was used for absorption measurements.

A Griffin flask shaker with a time switch served for extraction.

Procedure

To an aliquot of sample solution containing 1×10^{-5} M of titanium(IV), an adequate amount of hydrochloric acid, lithium chloride (2.5 M HCl, c(H, Li)Cl = 5 M), and sodium thiocyanate (c(NaSCN) = 1.5 M), was added, and the volume was made up to 5 mL. The solution was equilibrated with 5 mL CTMAB, CPC, or TDMAC (6×10^{-4} M) in chloroform or dichloromethane and the solutions were shaken mechanically in a 50-mL conical flask for 10 min. After the phases were separated by gravity, for each experimental point the absorbance of the organic phase was measured at 420 nm against a reagent blank solution.

A calibration graph was prepared with a solution containing 0.05–1.5 $\mu g\,mL^{-1}$ of titanium(IV) using a similar procedure.

Bauxite Analysis

A finely ground rock sample of about 100 mg of bauxite (NBS 69 a), was weighed and decomposed by heating in a Kjeldahl flask with 10 mL of acid mixture [water–conc. H_2SO_4–conc. HCl–conc. $HNO_3 = 20:10:3:1$ (v/v)]. The sample was decomposed three times. The solutions were evaporated slowly until fumes evolved, and then for 20–30 min. After cooling, solutions were diluted with deionized water (about 50 mL) and boiled to dissolve the salts. Finally, the hot solutions were filtered into a 100-mL standard flask, cooled, and made up to exact volume with deionized water.[22] Aliquots of the solutions were used for the determination of titanium by the above procedure.

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Aluminum Alloy Analysis

About 200 mg of aluminum alloy (Peschinée standard 0-636/02, containing 0.1% of titanium) was weighed in an Erlenmeyer flask and dissolved in a mixture of 4 mL of sulfuric acid (1 : 3) and 0.4 mL of hydrochloric acid (1 : 1). The sample was decomposed three times. The solutions were diluted with water to make 10 mL, passed into a 25-mL volumetric flask through a white ribbon filter, and washed with hot water. The solutions were cooled in the volumetric flask, water was added to the mark and stirred.[23] Aliquots of sample solutions were analyzed for titanium as described above.

RESULTS AND DISCUSSION

Optimum Conditions for Extraction and Spectrophotometric Determination of Titanium

The titanium(IV)–thiocyanate complex can be extracted with CPC, CTMAB, and TDMAC in chloroform or dichloromethane, from hydrochloric and sulfuric acid solutions. For simplicity sake, in all figures the results obtained by extraction of the titanium(IV)–thiocyanate complex with CPC into chloroform are presented.

Figure 1 shows the absorption spectra of the titanium(IV)–thiocyanate complex with CPC as a function of hydrochloric acid concentration, in the

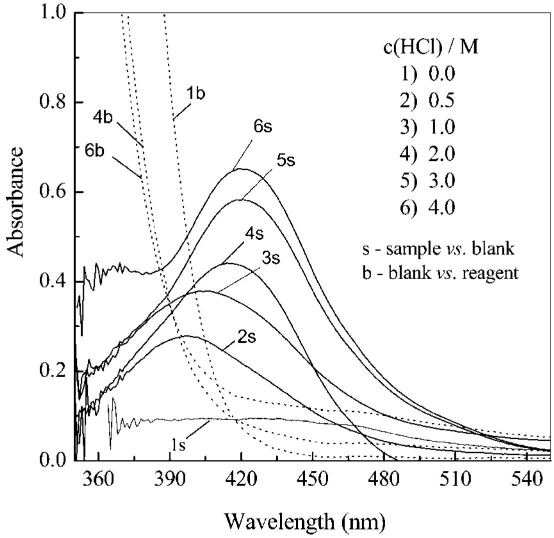

Figure 1. Dependence of the absorption spectra of titanium (IV)–thiocyanate complex on hydrochloric acid concentration. Conditions: 1×10^{-5} M Ti(IV), 1.5 M NaSCN, 1.5×10^{-2} M CPC in chloroform.

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presence of a sufficient excess of thiocyanate ions. The absorption maximum of the yellow extracted complex lies between 390 and 420 nm, its position and intensity depending on the acidity of the aqueous phase. At concentrations 2.5 M HCl and higher the constant maximum was reached at 420 nm. With constant ionic strength in the aqueous phase (c(H, Li)Cl = 3 M) before extraction, a maximum wavelength of 420 nm appeared already at 1 M HCl.

The results obtained with sulfuric acid were comparable. With an adequate excess of thiocyanate ions (1.5 M), and without the addition of chloride ions, the constant absorption maximum of 420 nm was attained in 2.5 M H_2SO_4. However, in 3 M H_2SO_4, the precipitate formed in the organic phase during extraction. Higher acidity produced even a larger amount of the precipitate and the organic phase had to be filtered before measurement. In the presence of a large excess of chloride ions (4 M), the position of maximum at 420 nm in the spectra was observed already at 0.8 M H_2SO_4.

Figure 2 shows the effect of mineral acid concentration on the absorbance of the organic layer after extraction of the titanium(IV)–thiocyanate complex with CPC dissolved in chloroform. The range examined was 0–6 M HCl and 0–5 M H_2SO_4. The maximum absorbance varied with the concentration of mineral acids and that of chloride ions. The maximum and constant absorbances were obtained in the range from 4 to 6 M HCl (Fig. 2a), if extraction

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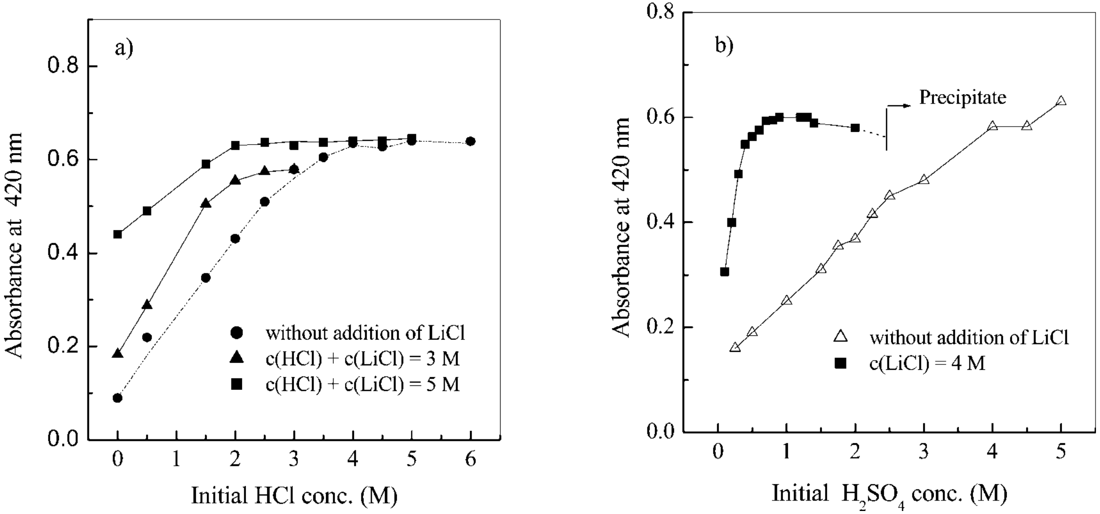

Figure 2. Dependence of the absorbance of extracted titanium(IV)–thiocyanate complex on hydrochloric (a) and sulfuric (b) acid concentration. Conditions: 1 × 10^{-5} M Ti(IV), 1.5 M NaSCN, 1.5 × 10^{-2} M CPC in chloroform.

was performed without constant ionic strength. Below 4 M HCl, full color development of the complex was not attained. When extraction took place from sulfuric acid solutions in the absence of chloride ions, there was no acidity range in which the absorbance of the organic phase was constant (Fig. 2b). Comparison of the curves in Fig. 2 shows that the effect of acidity on titanium extraction was highly dependent on the chloride concentration of the solution. Therefore at constant chloride concentration for the formation of the titanium(IV)–thiocyanate complex, the extraction at lower acidity was more efficient. Extraction from hydrochloric acid at constant ionic strength [c(H, Li)Cl = 5 M] yielded a maximum and constant absorbance at 2.0 M HCl and higher. Extraction from sulfuric acid solution in the presence of 4 M LiCl gave a maximum and constant absorbance in the range from 0.8 to 1.5 M H_2SO_4.

The results showed that the optimum hydrochloric acid concentration range was wider than that of sulfuric acid. Since precipitation did not take place below 6 M HCl, there was no need to filter the organic phase before measurement.

In order to optimize secondary ligands, the effects of chloride and sulfate on the extraction and spectrophotometric determination of titanium(IV)–thiocyanate with CPC, CTMAB, or TDMAC dissolved in chloroform were investigated. Figures 3 and 4 show relationships between the absorbance value and anion concentrations. From Fig. 3, it is evident that sensitivity increased with increase in the concentration of chloride ions. However, lower acidity required higher concentrations of lithium chloride in the investigated systems (Fig. 3a).

The addition of chloride ions to the solutions of the titanium(IV)–thiocyanate complex extracted from sulfuric acid solutions was accompanied by a significant increase in the complex absorbance. The best results were obtained at 1.25 M NH_4SCN and 2.2 M H_2SO_4 (Fig. 3b). Thus, as the optimum conditions for proper color development, 2.5 M LiCl was selected for the extraction from hydrochloric acid solutions, and 4 M LiCl for the extraction from sulfuric acid solution.

In contrast to this, if sulfate ion was added to the aqueous phase at different concentrations of hydrochloric acid, the absorbance values of the organic phase decreased with increase in sulfate concentration (Fig. 4a). With varying concentration of sulfate ions in the aqueous phase the absorbance of the organic layer decreased much less if the aqueous phase beside hydrochloric acid and sodium thiocyanate also contained chloride ions (curve 3). If extraction of the titanium(IV)–thiocyanate complex took place from hydrochloric acid solutions without the addition of chloride ions, the absorbance value decreased more rapidly at lower acidity and at lower concentrations of thiocyanate ions (curves 1 and 2). Sulfate ions reacted with cationic

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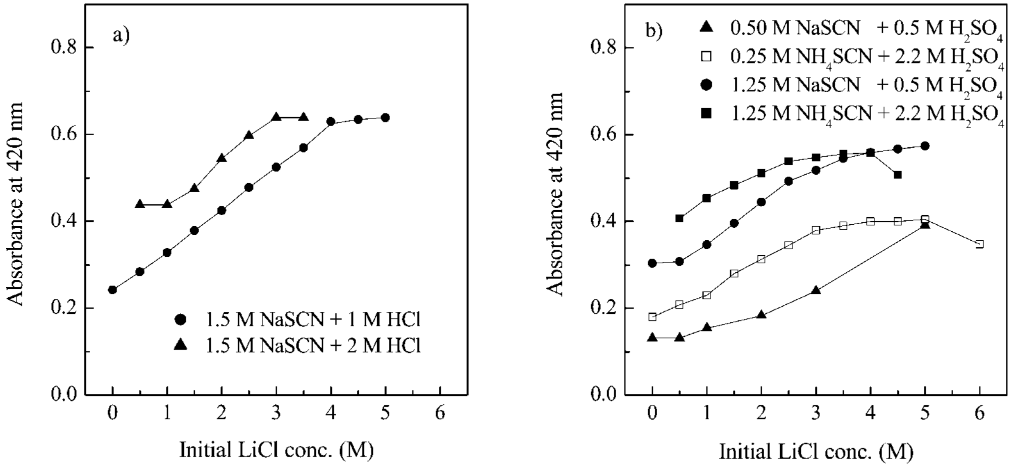

Figure 3. Dependence of the absorbance of extracted titanium(IV)–thiocyanate complex on lithium chloride concentration. Conditions: 1×10^{-5} M Ti(IV), 1.5×10^{-2} M CPC in chloroform.

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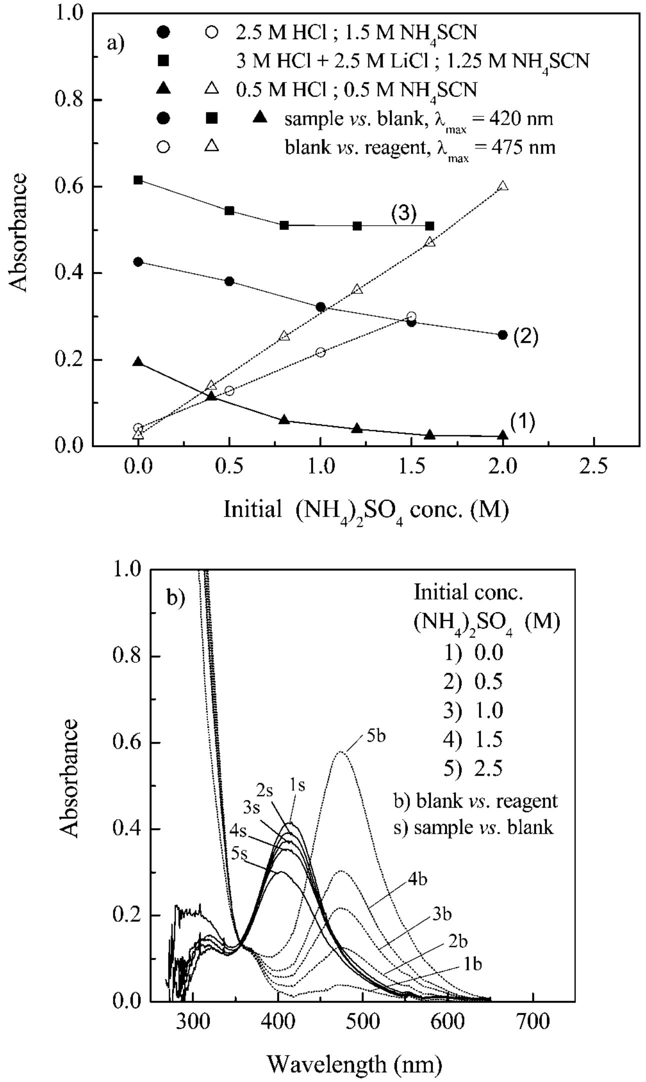

Figure 4. Dependence of the absorbance of extracted titanium(IV)–thiocyanate complex on ammonium sulfate concentration. Conditions: (a) 1×10^{-5} M Ti(IV), 1.5×10^{-2} M CPC in chloroform. (b) 1×10^{-5} M Ti(IV), 1.5×10^{-2} M NH_4SCN, 1.5×10^{-2} M CPC in chloroform.

surfactants (PAT) and formed a complex, thus consuming PAT for their own extraction and decreasing its concentration for the extraction of the titanium–thiocyanate complex. This is evident from the absorption spectra of reagent blank (Fig. 4b). In the absorption spectra of blank solutions with increased concentration of sulfate ions a new maximum was observed at 475 nm. On the other hand, an increase in chloride ion concentration had no effect on the position of the maximum in the absorption spectra of the blank organic phase. Thus, decolorization of the organic layer in the presence of sulfate ions in the aqueous phase could be attributed (1) according to Mari,[24] to the competition between the titanium(IV)–thiocyanate complex in the organic phase and titanium(IV)–sulfate complexes in the aqueous phase, (2) to lower concentration of thiocyanate ions in the aqueous phase due to an increase in the extraction of thiocyanic acid,[24] (3) to consumption of PAT for sulfate extraction in the organic layer.

The effect of thiocyanate concentration on the formation and extraction of the titanium(IV)–thiocyanate complex was examined. The results obtained with sodium and ammonium thiocyanate were almost identical. At zero thiocyanate concentration, the organic layer was colorless (Fig. 5a). For maximum extraction of the titanium(IV)–thiocyanate complex from 3 M hydrochloric acid with CPC a thiocyanate concentration in the range 2–3 M SCN (without LiCl added), and ≥ 1.0 M SCN (at 2.5 M LiCl) was required. If extraction took place from sulfuric acid, in the presence of 4 M LiCl, more thiocyanate was also needed (minimum 2 M) for maximum and constant absorbance of the organic phase (Fig. 5a). Titanium(IV) could be extracted with CPC with lesser thiocyanate excess, if extraction was carried out from hydrochloric acid solution containing an excess of chloride ions.

In order to confirm that both thiocyanate and chloride ions were constituents of the extracted species, titanium extraction from sulfuric acid media containing a constant sum of thiocyanate and chlorine ion concentrations [$c(NH_4SCN) + c(LiCl) = 4.5$ M] was studied. Results showed that titanium was poorly extracted if chloride concentration was lower (0.5 M LiCl) at simultaneously higher thiocyanate concentration (4 M NH_4SCN). The best results were obtained in the range 3–3.5 M LiCl with 1–1.5 M SCN (Fig. 5b).

The influence of extractant concentration in the organic phase on the extraction of the titanium(IV)–thiocyanate complex from the aqueous phase at optimum acidity (2.5 M HCl) and thiocyanate concentration (1.5 M NH_4SCN) was also studied in the presence of chloride (2.5 M HCl). For maximum extraction of titanium as a thiocyanate complex the molar ratio of CPC or TBMAC to titanium(IV) had to be at least 1000 : 1, and of CTMAB to titanium(IV) 330 : 1.

Different solvents were used for the extraction of the titanium(IV)–thiocyanate complex with the cationic surfactants. Results showed chloroform

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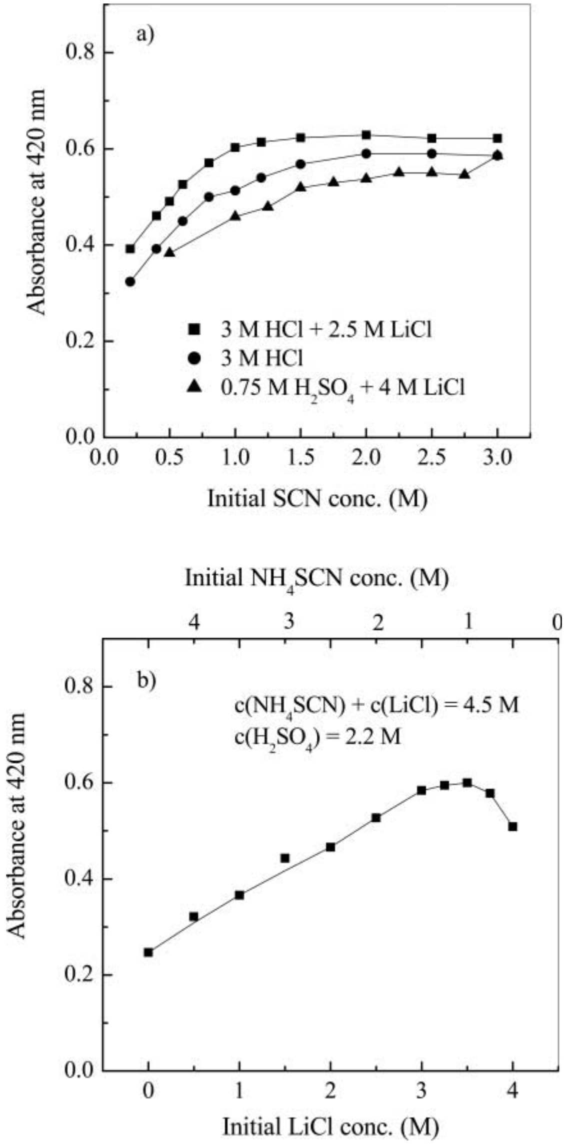

Figure 5. Dependence of the absorbance of extracted titanium(IV)–thiocyanate complex on thiocyanate and chloride concentration. Conditions: 1×10^{-5} M Ti(IV), 1.5×10^{-2} M CPC in chloroform.

and dichloromethane to be the best solvents. The solubility of the surfactants in methyl isobutyl ketone, *n*-hexane, and benzene, was a problem at higher concentrations. In isoamyl alcohol the extraction efficiency of the titanium(IV)–thiocyanate complex diminished. Chloroform was therefore selected for all other studies.

A 3-min shaking time was sufficiently long for the complex extraction. The absorbances were stable for at least 1 hr.

Under the optimum conditions Lambert-Beer's law was obeyed from 0.05 to 1.5 μg mL^{-1} titanium(IV). Table 1 shows calibration equations and detection limits. The limit of detection, was defined as $C_L = 3S_B/m$,[25] where C_L, S_B, and m are the limit of detection, standard deviation of the blank ($n = 11$), and the slope of the calibration graph, respectively. The precision of the method was tested on three sets of six samples each (at 2.5 M HCl, 2.5 M LiCl, 1.5 M NH_4SCN, 1.5×10^{-2} M CPC) containing 0.05, 0.5, and 1.0 μg mL^{-1} of titanium(IV). Relative standard deviations of the determination were 2.6%, 1.5%, and 1.1%, respectively.

The effects of foreign species, which are known to coexist with titanium, were investigated and the results obtained are shown in Table 2. An error in absorbance of $\pm 3\%$ was considered tolerable. Most anions and cations were tolerated in large quantities. The results show interference from tungsten(VI), molybdenum(VI), niobium(V), iron(III), tantalum(V), which increased the absorbance. It should be emphasized that with all the investigated reagents comparable analytical results were obtained.

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Composition of the Extracted Species

The ratio of titanium to CPC, CTMAB, and TDMAC was determined by Job's method of continuous variations. The composition of the complexes was determined by extraction of titanium(IV)–thiocyanate from 2.5 M hydrochloric acid media, in the presence of chloride. Two series of experiments were carried out for each cationic surfactant. The thiocyanate and chloride concentrations in the aqueous phase were kept constant and in a large excess. All results showed that the molar ratio of titanium to PAT was 1 : 2, regardless of the surfactant (Fig. 6). This was taken to confirm the presence in aqueous solutions of the anionic titanium–thiocyanate–chloride complex, bearing two negative charges.

As the ratio of titanium to thiocyanate or chloride could not be determined by the Job's method, the equilibrium shift method was used instead.[26] Results are presented in Table 3. The ratio of titanium was second power upon the thiocyanate ions, if extraction took place from the hydrochloric acid medium, and first power in the case of extraction from the sulfuric acid

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Table 1. Regression equations, correlation coefficients, standard deviation, and limit of detection.

Reagent	Optimum conditions	Regression equation	Correlation coefficient	Standard deviation (%)	C_L ng of Ti mL^{-1}
CPC	2.5 M HCl, 2.5 M LiCl, 1.5 M NaSCN	$A = 1.314\ C + 0.0156$	0.9998	1.02	19.8
CTMAB	2.5 M HCl, 2.5 M LiCl, 1.5 M NaSCN	$A = 1.217\ C + 0.0330$	0.9998	1.16	34.1
TDMAC	2.5 M HCl, 1.5 M LiCl, 1.5 M NaSCN	$A = 1.474\ C - 0.0038$	0.9989	1.64	35.3
CTMAB	1 M H_2SO_4, 4 M LiCl, 1.75 M NaSCN	$A = 1.257\ C + 0.0045$	0.9964	2.36	20.1

Note: C refers to Ti(IV) μg mL^{-1}; C_L refers to limit of detection.

Table 2. The effect of foreign ions on the spectrophotometric determination of titanium(IV) by proposed procedure.

Foreign ions	Concentration tolerated (molar ratio)
Na^{I}, K^{I}, Mg^{II}, sulphate, iodide, tartarate, citrate, bromide, acetate	5,000
Cd^{II}, Ca^{II}, perchlorate	2,500
Al^{III}, Zn^{II}, Mn^{II}, Ba^{II}, carbonate, phosphate	1,000
Cr^{III}, Li^{I}, NH_4^+, oxalate, EDTA	500
Ni^{II}	250
Co^{II}	100
Nitrate	50
Sc^{II}, Cu^{II}	10
Zr^{IV}, Hf^{IV},	5
W^{VI}, Fe^{III}, Ta^{V}, Mo^{VIa}, Nb^{Va}	1

Note: Conditions: 1×10^{-5} M Ti(IV), 2.5 M HCl, 2.5 M LiCl, 1.5 M NaSCN, 1.5×10^{-2} M CPC.
[a] 1×10^{-5} M EDTA present.

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medium. The dependence of the distribution ratio of titanium on initial chloride concentration was determined by keeping the sulfuric acid concentration constant at different chloride ions concentration. The dependences of 0.7-power at higher sulfuric acid concentration and 1.3-power at lower sulfuric acid concentration were obtained regardless of chloride concentration in the aqueous phase. These results indicate that the extraction of the titanium(IV)–thiocyanate species with CPC, CTMAB, and TMBAC from sulfuric acid media proceeded according to a complex extraction mechanism,

Table 3. Composition of the extracted titanium(IV)–thiocyanate species in different media by equilibrium shift method.

	Slope		
Medium	SCN	Cl	CPC
3 M HCl	1.9		1.9
3 M HCl + 2 M LiCl	2.1		2.0
0.75 M H_2SO_4 + 4 M LiCl	1.1		
0.5 M H_2SO_4 + 1.25 M NaSCN		1.3	
2.2 M H_2SO_4 + 1.25 M NH_4SCN		0.7	

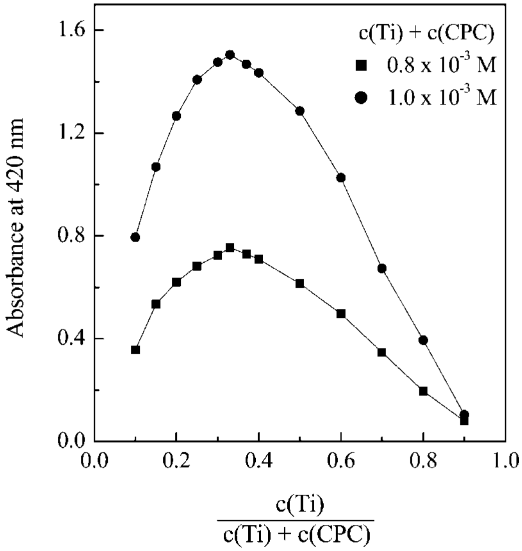

Figure 6. Job's method. Conditions: 2.5 M HCl, 2.5 M LiCl, 1.5 M NaSCN, 1.5×10^{-2} M CPC.

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depending on the sulfuric acid concentration ranges. The ratio of PAT to titanium agreed with that determined by the method of continuous variation.

The equilibrium shift method, like other methods for the determination of complex formation in solutions, was not suitable for analyzing chloride ions in the species extracted from hydrochloric acid media. Therefore, from the titanium to cationic surfactant and the titanium to thiocyanate ratios established by means of Job's method and the equilibrium shift method, it was presumed that the titanium(IV)–thiocyanate complex was extracted from hydrochloric acid media in the form of $[CP^+]_2[TiO(SCN)_2Cl_2]^{2-}$, $[CTMA^+]_2[TiO(SCN)_2Cl_2]^{2-}$, and $[TMBA^+]_2[TiO(SCN_2)Cl_2]^{2-}$.

Comparison with Other Methods

Titanium(IV) can be determined spectrophotometrically at trace concentrations by a variety of reagents (Table 4).[2–15] Compared with the other spectrophotometric methods, the present approach is more acceptable, because molar absorptivity was 4–10 times higher than with some other proposed methods.[2–8,13–15] Minimized polymerization and hydrolysis of titanium

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Table 4. Comparison of the proposed spectrophotometric determination of titanium and the other methods.

Reagent	Optimal acidity	λ_{max} (nm)	ε ($L\,mol^{-1}\,cm^{-1}$)	Reference
3-Hydroxy-2-methyl-1-(4-tolyl)-4-pyridone	HCl or $HClO_4$ (0.3–1.0 M) H_2SO_4 (0.5–2.0 M)	355	1.6×10^4	[2]
3,4-Dihydroxy-benzoic acid	pH 4–6	380	1.43×10^4	[3]
2,3-Dihydroxy-naphthalene	pH 4–9	375	3.2×10^4	[5]
6-(4-Nitrophenylazo)-3,4,5-trihydroxy-benzoic acid	pH 3.2–4.2	495	3.48×10^4	[6]
2,4-Dihydroxy-benzaldehyde isonicotinoyl hydrazone	pH 1–7	430	1.35×10^4	[7]
2-(2-Thiazolylazo)-*p*-cresol	pH 4–5.6	580	9.82×10^3	[8]
Tetraphenylarsonium or tetraphenylphosphonium chloride	HCl (2–3 M)	420	7.5×10^4	[12]
1-Phenyl-2methyl-3-hydroxy-4-pyridone	HCl (1.0–4.5M) H_2SO_4 (0.5–3 M)	365	2.65×10^4	[13]
Monooctyl-α-anilinobenzyl-phosphonate	H_2SO_4 (0.5 M) HCl (6.5 M)	336 420	1.1×10^4 2.2×10^4	[14]
N-hydroxy-*N*-*N*′-diphenylbenzamidine	pH 1.5	390	1.3×10^4	[15]
Cetyltrimethylammonium bromide	HCl (1.5–4.5 M), $\mu = 5\,M$	416	6.1×10^4	This work
Cetylpyridinium chloride	HCl (2–5 M), $\mu = 5\,M$	420	6.3×10^4	This work
Tetradecyldimethylbenzylammonium chloride	HCl (2–5 M), $\mu = 5\,M$)	417	7×10^4	This work

Note: Refs.[2–8] without thiocyanate ions, Refs.[12–15] in the presence of thiocyanate ions.

Table 5. Titanium determination in standard samples.

Standard	Found (%)	Certified content (%)
NBS 69 a (Bauxite)	2.80 ± 0.03[a]	2.8[a]
Peschinée 0-636/02 (aluminium alloy)	0.100 ± 0.002[b]	0.1[b]

Note: Other components—NBS 69 a: SiO_2, 6.00%; Al_2O_3, 55.00%; Fe_2O_3, 5.8%; ZrO_2, 0.18%; P_2O_5, 0.08%; V_2O_5, 0.03%; CaO, 0.29%; MgO, 0.02%; Na_2O, <0.01%; K_2O, <0.01; MnO, <0.01%; Cr_2O_3, 0.05%; BaO, 0.01%; SO_3, 0.04%. Peschinée: 0-636/02: Si, 1.40%; Fe, 0.57%; Cu, 0.10%; Mn, 1.00%; Cr, 0.05%, Ni, 0.01%; Zn, 0.10%; Sn, 0.010%.

[a] TiO_2.

[b] Ti.

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ion, which is usually observed at higher pH values[27] could be also due to the ability of PAT to extract titanium from acidic solutions.

Application of the Method

To check the applicability of the method, titanium was determined in reference samples (bauxite and aluminum alloy). The results as shown in Table 5 are in good agreement with the certified values.

CONCLUSION

Titanium(IV) reacts with thiocyanate in a highly acidic medium to give a complex extractable with CPC, CTMAB, or TDMAC in chloroform or dichloromethane. Hydrochloric acid medium is preferred because of the broader acidity range suitable for extraction. The presence of excess of chloride ions in the investigated systems was necessary for achieving maximum sensitivity. Relatively high molar absorptivity ($6{-}7 \times 10^4\,L\,mol^{-1}\,cm^{-1}$), short equilibration time, acceptable color stability, and low detection limits, make the proposed method superior to the earlier extractive spectrophotometric procedures. The applicability of the method, was tested on real reference samples. Good agreement with the certified values as well as good reproducibility of final results were achieved. Therefore, the proposed extractive spectrophotometric method for determining titanium(IV) as a mixed thiocyanate-chloride–PAT complex can be considered as a very useful, relatively simple, and reliable analytical method.

ACKNOWLEDGMENT

The authors are grateful to the Ministry of Science and Technology of Croatia for financial support to Research Project No. 0119641.

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Received September 1, 2003
Accepted April 6, 2004

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