CHAPTER IX

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM(IV)

RESUME

Extraction and spectrophotometric method for the determination of titanium(IV) is described. The titanium(IV) is extracted with α-phenyl-substituted hydroxamic acid into chloroform from strongly acidic solutions. The α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the synthesised hydroxamic acids which forms the yellow Ti-PTPMCHA complex having maximum absorbance at 375 nm with molar absorptivity 1.9×10^4 l $mol^{-1} cm^{-1}$. Various parameters for the optimum extraction conditions and the effect of thiocyanate to increase the sensitivity have been discussed.

INTRODUCTION

Hydroxamic acids have been used as analytical reagents for colorimetric determination of various metal ions (1-3). Several hydroxamic acids have been studied for the extraction and spectrophotometric determination of titanium(IV). (Table 1). It is observed that change in the substitution in the N- and C-phenyl ring of the hydroxamic acids, alter the sensitivity and selectivity of the reagent towards the metal ions. However, the increase in the side chain double bonds may sometime increase the selectivity and sensitivity of the metal ions. With this in view the nine new synthesised -phenyl-cinnamohydroxamic acids have been explored as better reagents for the extractions and spectrophotometric determination of titanium(IV). The sensitivity of the reagents has been increased by addition of thiocyanate as ternary complex.

TABLE 1

Comparison of spectrophotometric methods for the determination of titanium

Sr. No.	Hydroxamic acid	λ max	Molar absorptivity $l\ mol^{-1} cm^{-1}$	Ref.
1.	Benzo-	370	2,400	4
2.	N-Phenylbenzo-	380	6,700	5
3.	N-Phenylcinnamo-	400	10,200	6
4.	N-p-Tolyl-p-methoxy benzo-	410	5,700	7
5.	N-p-Chlorophenyl-3,4,5-trimethoxy-cinnamo-	380	17,000	8

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used were of AnalaR or GR grades of BDH and E. Merck, respectively, unless otherwise specified.

Hydroxamic acids

These are synthesised as described in Chapter II. 0.1% reagent solutions of hydroxamic acids in chloroform were used for extraction purposes.

Titanium solution

Standard titanium solution was prepared by heating 0.20 g of TiO_2 in a Pyrex flask with 8.0 g of ammonium sulphate and 25 ml of conc. sulphuric acid for 4 hrs. After cooling the resulting solution was transferred into a 250-ml volumetric flask containing 150 ml of water. The Pyrex flask was washed with 5% sulphuric acid and finally diluted with 5% sulphuric acid. The final concentration of titanium(IV) was determined volumetrically (9) and colorimetrically (5,10).

Thiocyanate solution

A 6.0 M solution of thiocyanate was prepared by dissolving required amount of ammonium thiocyanate in 500 ml of distilled water and standardised volumetrically(11).

APPARATUS

The spectral measurements were made on Shimadzu UV-VIS 240 spectrophotometer.

EXTRACTION PROCEDURE

Transfer an aliquot of Ti(IV) solution containing 38.5 ppm of metal into a separatory funnel and adjust the acidity of the aqueous phase to 9.5 M with conc. HCl and distilled water to final volume of 15 ml. Add 8 ml of 0.1% hydroxamic acid solution in chloroform and shake the contents for 10 min. Collect the organic layer in a 25-ml volumetric flask after drying over anhydrous sodium sulphate. Repeat the extraction with 2 ml of the reagent to ensure the complete recovery of the titanium and dilute the extracts upto the mark with chloroform. Measure the absorbance of the yellow coloured extract at 375 nm against the reagent blank prepared in the same manner.

Effect of thiocyanate

To study the ternary complex of Ti-hydroxamate and thiocyanate, add 1.0 ml of ammonium thiocyanate (6 M) solution to the mixture prior to the adjustment of the molarity of HCl and extract the complex as mentioned above.

RESULTS AND DISCUSSION

The spectral characteristics of titanium(IV) α-phenyl cinnamohydroxamic acids complexes are summarised in Table 2. From the preliminary studies, it is observed that N-p-tolyl-α-phenyl p-methoxy cinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the hydroxamic acids studied here. Hence the optimum conditions for the extraction and spectrophotometric determination of titanium with PTPMCHA has been investigated.

Effect of acidity

The extraction of titanium was studied in different molarities of hydrochloric acid. The results recorded in Table 3 show that there is very poor extraction below 7 M HCl concentration. The extraction starts at 8.0 M HCl and is quantitative between 9.0 M and 10.0 M HCl. The maximum extraction is obtained in the range of 9.2 - 9.8 M HCl and hence all the extractions were made at 9.5 M HCl concentration.

Effect of reagent concentration

Extraction of titanium(IV) was studied with varying the concentration of N-p-tolyl-α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA). 10 ml of 0.1% (w/v) reagent solution in chloroform is sufficient for the quantitative

TABLE 2

Spectral characteristics of titanium-substituted cinnamohydroxamic acid complexes

Ti(IV) : 1.54 ppm

Molarity : 9.5 M HCl

Hydroxamic acid : 0.1%, 10 ml in $CHCl_3$

Solvent : $CHCl_3$

Shaking time : 10 min

Compd No.	Cinnamohydroxamic acid	λmax nm	Colour of Complex	Molar absorptivity l mol^{-1} cm^{-1}	Sandell's sensitivity $\mu g\ cm^{-2}$
I	N-Phenyl-α-phenyl-p-methoxy-	375	Yellow	1.7×10^4	0.0028
II	N-p-Tolyl-α-phenyl-p-methoxy-	375	Yellow	1.9×10^4	0.0025
III	N-m-Tolyl-α-phenyl-p-methoxy-	375	Yellow	1.8×10^4	0.0027
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	375	Yellow	1.6×10^4	0.0030
V	N-Phenyl-α-phenyl-	355	Yellow	1.2×10^4	0.0040
VI	N-p-Tolyl-α-phenyl-	355	Yellow	1.3×10^4	0.0037
VII	N-m-Tolyl-α-phenyl-	355	Yellow	1.3×10^4	0.0037
VIII	N-p-Chlorophenyl-α-phenyl-	355	Yellow	1.1×10^4	0.0044
IX	N-Phenyl-α-phenyl-3,4,5-trimethoxy-	375	Yellow	1.6×10^4	0.0030

TABLE 3

Effect of acidity on the extraction of titanium(IV)

Ti(IV) : 1.54 ppm

PTPMCHA : 0.1%, 10 ml in $CHCl_3$

Shaking time : 10 min

Solvent : $CHCl_3$

λmax : 375 nm

Colour of Complex: Yellow

Molarity of HCl	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
8.0	1.3×10^4	70
8.5	1.6×10^4	84
9.0	1.8×10^4	96
9.2	1.9×10^4	100
9.5	1.9×10^4	100
9.8	1.9×10^4	100
10.0	1.8×10^4	96
10.5	1.5×10^4	81
11.0	*	*

* The extract becomes turbid.

extraction of the titanium(IV). The higher reagent concentration can be used without any difficulty.

Stability of the colour and extraction time

Titanium complex is stable for several days. Extraction of the titanium is very rapid under the recommended conditions in the analytical procedure. Shaking time for 10 min was enough to obtain the equilibrium when the reagent was added to the aqueous phase.

Beer's law

Beer's law is obeyed in the range of 0.15 to 3.1 ppm of titanium. The molar absorptivity is 1.9×10^4 l $mol^{-1} cm^{-1}$ at 375 nm. The Sandell's sensitivity is 0.0025 $\mu g/cm^2$.

Effect of ammonium thiocyanate

The sensitivity of the method is enhanced by the use of thiocyanate for the extraction of titanium with hydroxamic acid as Ti-PTPMCHA-SCN ternary complex. The results indicate that a maximum of 1.0 ml ammonium thiocyanate (6 M) is sufficient for the ternary complex formation. The molar absorptivity of Ti-PTPMCHA-SCN complex is 2.9×10^4 l $mol^{-1} cm^{-1}$ at 375 nm.

TABLE 4

Effect on cations and anions on the extraction of titanium(IV)

Ti(IV) : 1.54 ppm
PTPMCHA : 0.1%, 10 ml in $CHCl_3$
Shaking time : 10 min
Molarity : 9.5 M HCl
Solvent : $CHCl_3$
λmax : 375 nm
Colour of Complex : Yellow

Ions	Added as	Amount added (mg)	Absorbance
Ag^{+}	$AgNO_3$	25	0.62
Cd^{2+}	$CdSO_4$	30	0.62
Pb^{2+}	$Pb(NO_3)_2$	30	0.63
Be^{2+}	$BeSO_4$	30	0.62
Mg^{2+}	$MgSO_4$	30	0.62
Ca^{2+}	$Ca(NO_3)_2$	30	0.62
Ba^{2+}	$BaCl_2$	25	0.61
Sn^{2+}	$SnCl_2$	25	0.61
Co^{2+}	$CoCl_2$	25	0.62
Cu^{2+}	$CuSO_4$	30	0.63
Hg^{2+}	$HgCl_2$	25	0.62
Ni^{2+}	$NiCl_2$	20	0.62
Zn^{2+}	$ZnSO_4$	30	0.62
Mn^{2+}	$MnCl_2$	20	0.61
Cr^{3+}*	$CrCl_3$	20	0.62
Al^{3+}	$AlCl_3$	30	0.62
V^{5+}*	NH_3VO_3	25	0.62
Mo^{6+}*	$(NH_4)_6Mo_7O_{24}$	10	0.62
Zr^{4+}*	$Zr(NO_3)_4$	5	0.61
Cl^{-}	NaCl	30	0.61
Br^{-}	NaBr	15	0.62
I^{-}	NaI	20	0.62

* Masking agent used

Effect of diverse ions

Titanium was determined in the presence of large number of diverse ions (Table 4). Moderate amounts of various metal ions and anions commonly associated with titanium were tolerated except chromium, vanadium, molybdenum, zirconium and fluoride which are interfering. The interferences of vanadium was eliminated by adding $FeSO_4$ while the molybdenum was removed by precipitation with sulphide, prior to the extraction.

Composition of the complex

The stoichiometric composition of the Ti:PTPMCHA complex was determined by the slope ratio method (12). The stoichiometry of Ti-PTPMCHA complex was determined by taking fixed amount of titanium and gradually increasing the amount of reagent (L_1). The slope of the plot of log D_M vs - log (L_1) was found to be 2.0, confirms the metal to ligand (L_1) ratio 1:2, and 1:2:1 for the ternary. Ti-PTPMCHA-SCN complex.

$$TiOCl_2 + 2HA \xrightarrow{HCl} (TiOCl\ A_2)^- + 2\ H^+ + Cl^-$$

$$(TiOCl\ A_2)^- + SCN^- \xrightarrow{HCl} (TiOA_2\ SCN^-)\ H^+ + 2Cl^-$$

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