Trade Science Inc.

March 2010 ISSN : 0974-7419 Volume 9 Issue 1

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 9(1) 2010 [141-144]

A sensitive spectrophotometric method for the determination of titanium (IV) using gallacetophenone phenylhydrazone with applicatin to ilmenite

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Received: 25th January, 2010 ; Accepted: 4th February, 2010

ABSTRACT

The spectrophotometric determination of titanium (IV) using gallacetophenone phenylhydrazone (GPPH) is a sensitive and fairly selective method when compared to other spectrophotometric methods. Titanium (IV) is determined by measuring the absorbance of the orange colored complex at 375 nm in the pH range 2.3-2.8. Beer's law is obeyed over the range 0.1-1.2 μg ml^{-1}. The molar absorptivity and the Sandell's sensitivity of the complex are found to be 3.254×10^4 l mol^{-1}cm^{-1} and 0.0015 μg cm^{-2} respectively. The stoichiometry of the complex as determined by job's continuous variation and Asmus methods is 1:2 (metal:ligand) and its stability constant at 30^{0}C is 2.73×10^7. The method is applied for the determination of titanium in ilmenite.

KEYWORDS

Titanium (IV) determination;
Spectrophotometry;
Molar absorptivity;
Gallacetophenone
phenylhydrazone;
Ilmenite.

INTRODUCTION

The most common spectrophotometric reagents employed for the determination of titanium (IV) are hydrogen peroxide[1] and tiron[2]. However, N-benzoyl-N-phenylhydroxylamine[3,4] and N-phenyllaurohydroxamic acid[5] are introduced for extractive spectrophotometric determination of titanium (IV). Aroylhydraones such as pyridoxal salicyloylhydrazone[6], diphenylglyoxal bis (benzoylhydrazone)[7] and dipyridylglyoxal bis (benzolyhydrazone)[7], salicylaldehyde 2-methyl isonicotinoylhydrazone[8], 1,2-cyclohexanedione bis (benzoylhydrazone)[9] are also extensively employed for the spectrophotometric determination of titanium. Sane et al[10] have developed a spectrophotometric method using 5,6-dibromogallacetophenone as a reagent. The hydrazones employed, so far, though reasonably sensitive are less selective. Titanium is ninth most abundant element and it has excellent corrosion resistance, especially sea water. Titanium is important in the manufacture of steel as a carbon and nitrogen stabilizing element to inhibit intergranular corrosion. Its oxide, TiO_2 is inert and non toxic and used in cosmetic and pharmaceutical industries. In view of its importance, the usefulness of gallacetophenone phenylhydrazone for the spectrophotometric determination of titanium (IV) is investigated in detail and applied to the analysis of ilmenite.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade, unless stated otherwise. Standard Titanium (IV) solution was prepared by taking about 2.0g of titanium dioxide. It was accurately weighed and fused with potassium pyrosulphate in a platinum crucible. The melt was extracted into 1M sulphuric acid. The solution was standardised gravimetrically with cupferron[11]. Working solutions were prepared by appropriate dilution of the stock solution. Gallacetophenone phenylhydrazone was prepared as per the standard procedure given by Blatt[12] and Curniss et al[13]. The molecular formula of the compound is $C_{14}H_{14}N_2O_3$ and it melts at 146-147^{0}C. The reagent solution (2.5 X 10^{-3}M) was prepared in 95% ethanol just before use. Sodium acetate buffer of pH 2.5 was prepared from 10% sodium acetate and 0.5M sulphuric acid.

Apparatus

Recording spectrophotometer model SHIMADZU UV-240 and Elico digital pH meter model LI-120 were used in the present investigation.

Procedure

An aliquot of solution containing 1.2 μg of Ti/ml was transferred into a clean beaker. 5.0ml of 2.5 X 10^{-3}M GPPH solution (i.e. ten fold excess) were added. The pH of the solution was adjusted to 2.5 by the addition of 10% sodium acetate solution. The contents of the beaker were transferred into a 50-ml standard flask and diluted to the mark with ethanol. The ethanol concentration was maintained at 30% V/V and then the absorption spectrum of the complex recorded against the reagent blank. Similarly, the absorption spectrum of the reagent was recorded using ethanol as blank. The absorption spectra of the reagent and Ti (IV)-GPPH complex are shown in Figure 1. It is seen that the complex has λ_{max} at 375 nm and the reagent has a weak absorption at this wavelength. Hence absorbance measurements have been made at 375nm.

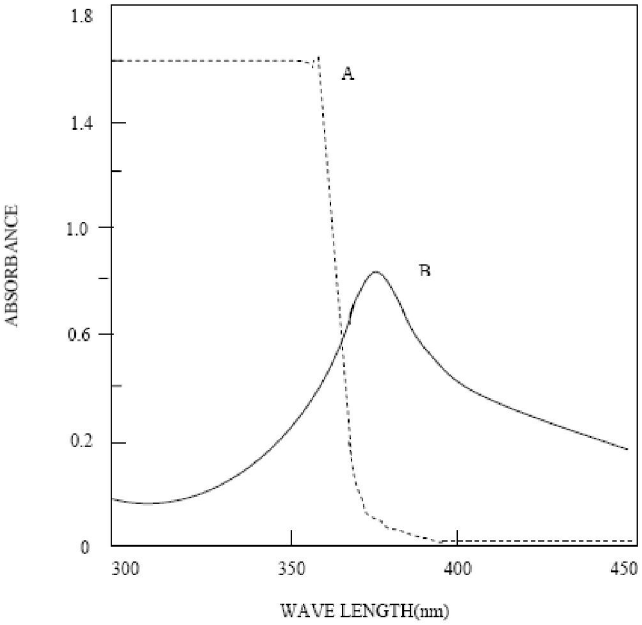

Figure 1 : A. Absorption spectra of GPPH and B. Ti(IV)-GPPH complex

Effect of pH, reagent concentration

The determination of titanium (IV) was studied over the pH range 1.5-3.5. The absorbance of the complex was maximum and constant in the pH range 2.3-2.8. At optimum pH, absorbance measurements were carried out by varying the reagent concentrations. It is observed that the addition of a 10-fold excess of reagent is sufficient for maximum and constant absorbance.

RESULTS AND DISCUSSION

Beer's law range, sensitivity and reproducibility

A straight line passing through the origin was obtained between absorbance and concentration of titanium in the range 0.1-1.2 μg ml^{-1}, thus obeying Beer's law. The optimum concentration range as per Ringbom plot was 0.3-1.0 μg of Ti/ml. The molar absorptivity and the Sandell's sensitivity are 3.254 X 10^{4}l mol^{-1} cm^{-1} and 0.0015 μg cm^{-2} respectively. The reproducibility was good and the standard deviation for a set of ten measurements of 1.0 μg ml^{-1} of Ti(IV) was 0.008 μg.

Composition of the complex

The composition of the complex was arrived at by Job's continuous variation and Asmus methods. In Job's method the graph plotted between mole fraction of the reagent and absorbance shows that each mole of the metal ion reacts with two moles of the reagent. In Asmus method plots drawn between l/V, l/V^2, l/V^3 values and l/m (Figure 2) where V is total volume of the solution and M is the extinction modulus, reveal the formation of 1:2 complex between Ti(IV) and GPPH which is in conformity with the above method. The stability constant of the complex calculated from the Asmus method was found to be 2.73 X 10^7 at 30^{0}C.

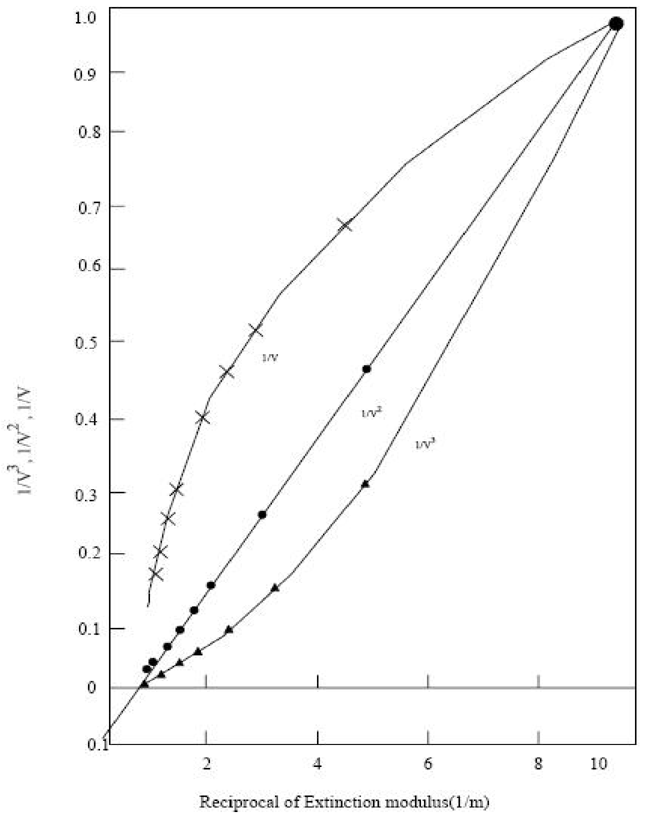

Figure 2 : Composition of Ti(IV)-GPPH complex by Asmus method

The formula of the complex may be written as $TiO(GPPH)_2$. However, it is well known that all the oxotitanium species are not monomers. For example, $TiO(acac)_2$ is found to be dimeric[14] and other simple oxotitanium compounds such as $TiOSO_4$. H_2O and $TiOX_2$ (X = F, Cl, Br or I) are polymeric[14]. In the present complex also, polymerisation cannot be ruled out.

Effect of foreign ions

The effect of foreign ions in the determination of 1.0 μg ml^{-1} of titanium(IV) was studied. The tolerance limit was taken as the amount required to cause ± 2% error in the absorbance. The tolerance limits of the ions are given in the TABLE 1. Only a few cations like Mo(VI), V(V), W(VI) interfere seriously. The interference of Cu(II) can be masked using sodium thiosulphate. The interference of aluminium (III) is not serious. Considerable amounts of Al(III) i.e. (10-fold excess) can be tolerated when the determination is carried out at lower pH 2.0-2.3. Among the anions tested fluoride, oxalate, citrate, tartrate, EDTA and phosphate interfere seriously in the determination by bleaching the color.

TABLE 1 : Effect of foreign ions on the determination of 1.0 μg ml^{-1} of Ti

Ion added	Tolerance limit. μg ml^{-1}	Ion added	Tolerance limit. μg ml^{-1}
Al(III)*	10	W(VI)	Nil
Be(II)	20	Zn(II)	50
Ca(II)	100	Br^-	100
Co(II)	50	Cl^-	100
Cr(III)	50	$C_2O_4^{2-}$	Nil
Cu(II)**	20	Citrate	Nil
Fe(II)	20	EDTA	Nil
Fe(III)	20	F^-	Nil
Mg(II)	100	I^-	50
Mn(II)	50	NO_3^-	100
Mo(VI)	Nil	$H_2PO_4^-$	Nil
Ni(II)	50	SO_4^{2-}	100
Pb(II)	50	$S_2O_3^{2-}$	100
U(VI)	20	SCN^-	50
V(V)	Nil	Tartrate	Nil

* At pH 2.3
** In the presence of $S_2O_3^{2-}$.

Determination of titanium in ilmenite

The proposed method was applied for the determination of titanium(IV) in ilmenite. About 100 mg of the powdered ore was weighed accurately, transferred to a platinum crucible and treated with 10ml of a mixture of sulphuric acid and hydrofluoric acid (1:5) and a few drops of nitric acid. It was evaporated to the fumes to expel HF. The residue was treated with a little H_2SO_4 and the solution made upto 100ml[15]. The solution further diluted to get lower concentrations. An aliquot of this solution was treated with 5.0ml of 2.088 X 10^{-3}M reagent solution. The pH of the solution was maintained at 2.3 by adding 10% sodium acetate solution and the absorbance of the complex measured at 375nm. The amount of titanium present in the ore was found to be 24.64% (n=3) which was in near agreement with 24.4% (n=3) as obtained from the standard hydrogen peroxide procedure[16].

CONCLUSIONS

The results show that gallacetophenone phenylhydrazone is a fairly sensitive and selective reagent for the determination of titanium (IV). It is more sensitive than tiron ($\in$=1.59 X 10^4 l mol^{-1} cm^{-1}). The determination of titanium (IV) in the presence of considerable amounts of iron and aluminium makes it suitable for the analysis of titanium when present in rocks, minerals and silicious material. The comparative advantages of the reagent are given in TABLE 2.

TABLE 2 : Comparison of the spectrophotometric methods of determination of titanium.

Reagent	λ max nm	pH / Acidity	Molar absorptivity l mol^{-1} cm^{-1} × 10^3	Interfering ions
Hydrogen peroxide	410	Dil. H_2SO_4	0.7	Fe(III), Mo(VI), V(V), U(VI), F^-, $C_2O_4^{2-}$, Citrate
Tiron	390	4.3-9.6	15.9	Fe(III), Al(III), Cu(II), U(VI), Mo(VI), Zr(IV), V(V)
N-Benzoyl-N-Phenyl hydroxylamine	340	1.7-1.85	5.0	Fe(III), V(V), Mo(VI)
Pyridoxal salicyloyl hydrazone	390 440	0.9-2.5	5.5 3.9	Mo(VI), W(VI), Cr(III).F^- -
Diphenylglyoxal bis (benzoylhydrazone)	520	4.7	0.81	-
Dipyridylglyoxal bis (benzoylhydrazone)	395 470	4.7	8.9 2.4	- -
Salicylaldehyde 2-methyl isonicotinoyl hydrazone	425	1.8-3.8	4.4	-
1,2-Cyclohexanedione bis (benzoylhydrazone)	477	1.8-3.0	10.5	Ca(II), Zn(II), Hg(II), Pb(II), As(III), Co(II), Al(III), Cd(II)
5,6-dibromo gallacetophenone	390	3.0	1.75	V(V), Zr(IV), Th(IV), Fe(II), U(VI)
Gallacetophenone phenylhydrazone	375	2.3-2.8	32.5	Mo(VI), W(VI), V(V), F^-, $C_2O_4^{2-}$, Citrate, $H_2PO_4^-$, EDTA

ACKNOWLEDGEMENT

The authors thank the University Grants Commission, New Delhi, for financial assistance to one of them (D.V.Reddy)

REFERENCES

[1] A.Weissler; Ind.Eng.Chem.Anal.Ed., **17**, 695 **(1945)**.

[2] J.H.Yoe, A.R.Armstrong; Anal.Chem., **19**, 100 **(1947)**.

[3] S.C.Shome; Analyst, **85**, 452 **(1960)**.

[4] H.Ishii, H.Einaga; Bunseki Kagaku, **17**, 976 **(1968)**.

[5] H.D.Gunawardhana; Analyst, **108**, 952 **(1983)**.

[6] M.Gallego, M.Valcarcel, M.Garcia-Vargas; Mikrochim.Acta, **1**, 289 **(1983)**.

[7] M.Silva, M.Gallego, M.Valcarcel; Talanta, **27**, 615 **(1980)**.

[8] A.V.Dolgorev; Zh.Anal.Khim., **28**, 1093 **(1973)**.

[9] M.Garcia-Vargas, S.Trevilla, M.Milla; Talanta, **33(3)**, 209 **(1986)**.

[10] R.T.Sane, K.D.Deodhar, P.N.Trakru, V.S.Brukule; J.Indian Chem.Soc., **85(5)**, 511 **(1978)**.

[11] L.Erdey; 'Gravimetric Analysis', Pergamon Press, London Part-2, 461 **(1965)**.

[12] A.H.Blatt; 'Organic Synthesis', John Willey, Coll **2**, 304 (1943) **(1945)**.

[13] B.S.Curniss, A.J.Hannaford, V.Rogers, P.W.G.Smith, A.R.Tatchell; 'Vogel's Test Book of Practical Organic Chemistry', 4th ed ELBS and Longman, London, 886 **(1978)**.

[14] J.C.Bailar, H.J.Emeleus, R.Sir Nyhlom, A.F.Trotman-Dickenson; 'R.J.H.Clark's Comprehensive Inorganic Chemistry', Pergamon Press, London, **3**, 377 **(1973)**.

[15] I.B.M.; Manual of Procedures for Chemical and Instrumental Analysis of Ores, Minerals and Ore Dressing Products, 163 **(1979)**.

[16] J.Basset, R.C.Denny, G.H.Jeffery, J.Mendham; 'Vogel's Text Book of Quantitative Inorganic Analysis', ELBS and Longman, London, 750 **(1978)**.