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SPECTROPHOTOMETRIC DETERMINATION AND LIQUID – LIQUID EXTRACTION AND COMPARATIVE STUDY OF Zr (IV) AND Ti(IV) WITH N,N'BIS (O-HYDROXY ACETOPHENONE) ETHYLENE DIIMINE DERIVATIVE AS AN ANALYTICAL REAGENT

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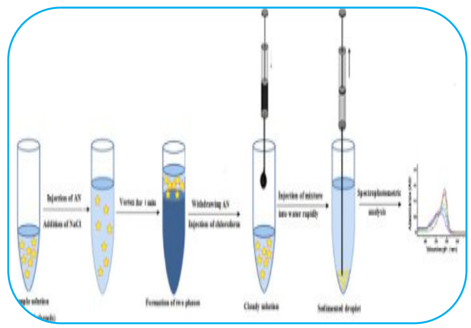
ABSTRACT

Solvent extraction is considered to be one of the best methods of separation. It is based on transfer of a solute from one phase to another, which is immiscible with each other. The main reason for its usefulness among these separation techniques is because of its ease, simplicity, speed, wide scope, utilizing apparatus and requirement of only a separating funnel, application both to trace and macro level of metals. Separation of heavy metals from the environment can be possible by using this method.

The spectrophotometric method is coupled with solvent extraction technique and used for the determination and comparative study of Zr(IV) and Ti(IV) using N,N'bis(O-hydroxy acetophenone) ethylene diimine(HAPED) as an analytical reagent. This reagent is synthesized in the laboratory and characterized by NMR, IR, Mass and elemental analysis for its purity. This reagent forms a light pink colored stable complex with Zirconium metal and light yellow colored stable complex with Titanium metal, which can be quantitatively extracted into chloroform at pH 7.8 and pH 5.6 respectively. This Zr(IV)-HAPED complex in chloroform exhibit intense absorption peak at 530nm and Ti(IV) –HAPED complex in chloroform gave intense absorption peak at 500nm. Beer's law is obeyed in the range of 1 to 10 ppm of Zirconium and Titanium solution giving linear and reproducible graph.

The Molar absorptivity and Sandell's sensitivity are also calculated. However, the effect of reagent concentration, equilibrium stability and effect of interfering ions have been studied. The Stoichiometric ratio of complex of Zirconium and Titanium studied by Job's Continuous Variation method, Mole ratio and Slope ratio method have been studied and it is found to be metal and ligand ratio is 1:2. The proposed method is rapid, sensitive, reproducible, accurate and has been satisfactory applied for determination and separation of Zr(IV) and Ti(IV) in commercial mixtures, pharmaceutical samples and alloys.



KEYWORDS: *N,N'bis(O-hydroxy acetophenone) ethylene diimine (HAPED) reagent, Zirconium(IV), Titanium(IV), Sandell's Sensitivity, Molar absorptivity, Spectrophotometric determination.*

INTRODUCTION

The name of Zirconium is taken from the mineral Zircon. Zirconium is mainly used as a refractory and opacifier, although it is used in small amounts as an alloying agent for its strong resistance to corrosion[1-2]. It forms a variety of inorganic and organometallic compounds such as zirconium dioxide and zirconocene dichloride respectively[3-4]. In powder form Zirconium is highly flammable but the solid form is far less prone to ignition. Zirconium is highly resistant to corrosion by alkalis, acids, salt water and other agents[5-6]. However, it will dissolve in hydrochloric and sulfuric acid especially when fluorine is present. Alloys with zinc become magnetic below 35k[7-8]. Zirconia is also a component in some abrasives, such as grinding wheels and sandpaper. High temperature parts such as combustors, blades and vanes in jet engines and stationary gas turbines are to an increasing extent being protected by thin ceramic layers. Titanium and titanium alloys are characterized by excellent mechanical properties, high toughness, high strength and relatively low weight. Moreover titanium shows great corrosion resistance in many environments, high biocompatibility, and also some titanium alloys show good heat resistance[9-11]. Thus the combination of these properties and characteristics of titanium alloys have led to successful application switch demand high level of reliable performance mainly in aerospace, military, automotive, chemical and power plant, petroleum and also in surgery and medicine, as well as in many other industries.

Extractive methods [12-13] are highly sensitive but generally lacks in simplicity. Spectrophotometry is essentially a trace- analytical technique and is one of the most powerful tools in chemical analysis. A wide variety of reagents have been proposed for the spectrophotometric determination of Zirconium and Titanium. The extractive spectrophotometric analysis enables to separate desired metal ion, which is to be estimated in presence of other metal from samples. In the present work a novel analytical reagent N,N'bis''(O-hydroxy acetophenone) ethylenediimine (HAPED), was used for the extractive spectrophotometric determination of Zirconium and Titanium. The developed method can be employed for efficient determination of Zirconium and Titanium at microgram level. The results of analysis obtained were compared with those obtained by known methods[14-16].

MATERIALS AND METHODOLOGY

1. Instruments:

Shimadzu 2,100 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustment.

2. Synthesis of Reagent

The HAPED reagent was synthesised by O-hydroxy acetophenone and ethylene diamine in methanol in 2:1 molar proportions are mixed in round bottom flask. Shake the flask for 10 to 15 min. Immediately, dark-yellow-colour solid is obtained which is poured in ice-cold water. The solid obtained is separated by filtration and washed with cold water and the product is recrystallised from ethanol. The yield was about 90%. It is then characterised and used for extractive spectrophotometric determination of Zr(IV) and Ti(IV). A stock solution of HAPED reagent with concentration 0.1% was prepared in methanol. The scheme of reaction is shown in Figure 1.This is less hazardous synthesis as less amount of solvents are used in this method. Separation of metals can be takes place at very low concentration at micropgram or nanogram level. No sophisticated instruments are required for this method of analysis. Hence this type of research shows green chemistry approach.

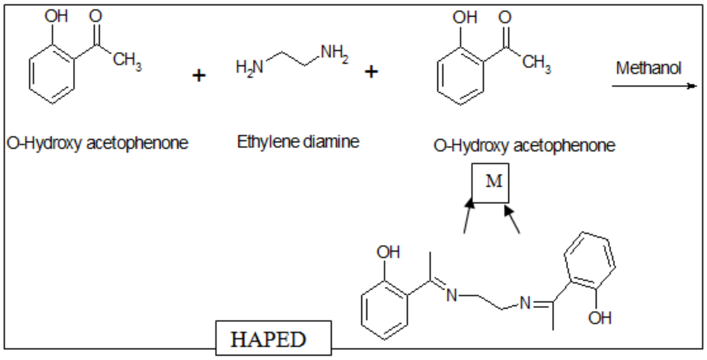


Figure-1:-Synthesis of reagent N,N"-bis (O-hydroxy-acetophenone) ethylene diimine (HAPED)

3. Preparation of stock solution

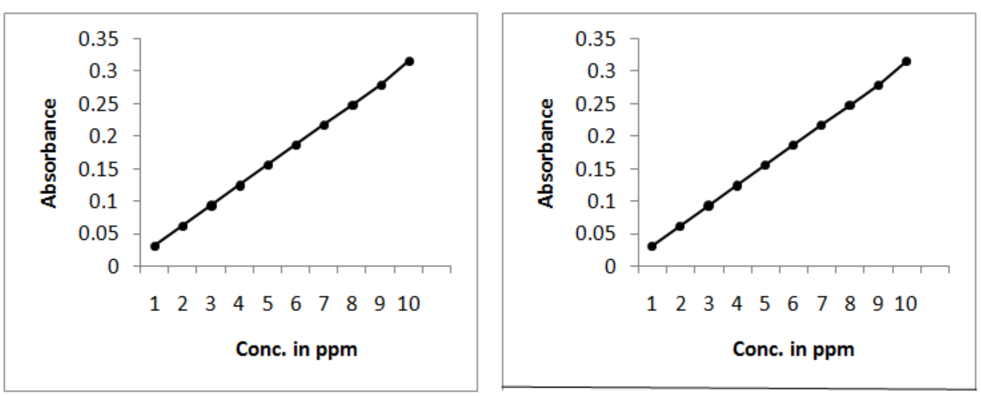
A weighed quantity of Zirconium Nitrate and Titanium Chloride was dissolved in double distilled water containing dilute Nitric acid and hydrochloric acid respectively and then diluted to desired volume by double distilled water. The solution was then standardized with titrimetric method method.

4. Recommended procedure

Mix 1-cm^3 aqueous solution containing 1-100mg of Zirconium and Titanium and 2 cm^3 of 0.1% methanolic solution of HAPED reagent in 25 cm^3 beaker. Adjust the pH of the solution to required value with buffer solution Make the final volume 10cm^3. Transfer the solution into 125 cm^3 separate funnel and equilibrate for 1min. with 10cm^3chloroform. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 370 nm against reagent blank.

5. Preparation of calibration plot

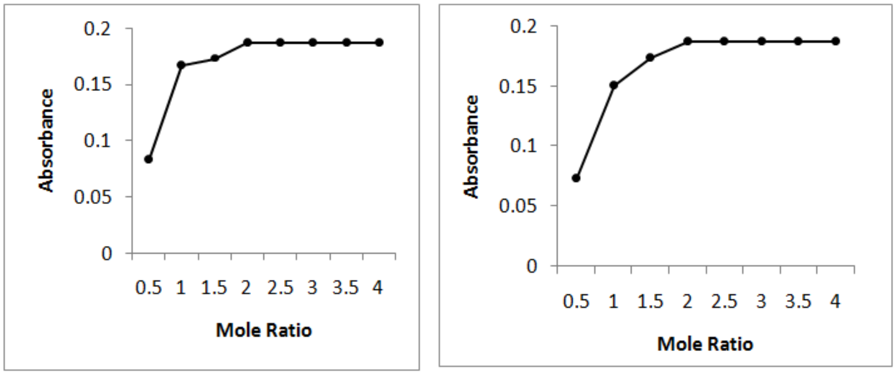
The calibration curve is prepared by taking known amount of Zirconium and Titanium which is described in the procedure. A graph of absorbance against concentration is shown in Figure 2. The concentration of the unknown Zirconiumand Titanium solutions is determined from the calibration plot.



Figure,.2: Calibration plot for extractive spectrophotometric determination of Zr(IV) and Ti(IV) with chloroform.

6. Composition of the extracted species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Zr(IV) and Ti(IV)- HAPED regent is 1: 2 which is represented in Figure 3.



Figure,3e Composition of the Extracted Zr(IV) and Ti(IV)- HAPED species by mole ratio method

7. Effect of foreign ions:

Various cations and anions were investigated to find the tolerance limit of these foreign ions in the extraction of Zirconium (IV) and Titanium(IV) presented in Table 2. The effect of diverse ions on the Zirconium (IV)and Titanium(IV) determination was studied, in presence of a definite amount of a foreign ion. The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Zirconium(IV)and Titanium(IV). The ions which interfere in the spectrophotometric determination of Zirconiumand Titanium were masked by using appropriate masking agents presented in Table 3.

Table :1

Sr. No.	Different parameters Studied	Observation for Zirconium(IV)	Observation for Titanium(IV)
1	Solvent	Chloroform	Chloroform
2	pH	7.8	5.6
3	Equilibrium time	1 min.	1 min.
4	Stoichiometry M:L	1:2	1:2
5	95% confidence limit	±0.2462	±0.2560
6	Reagent Conc.	0.1%	0.1%
7	Volume of Rgt.	$2cm^3$	$2cm^3$
8	Average of 7 determination	9.98	9.50
9	Stability of the complex	46 h.	40 h.
10	Sandell sensitivity	0.0318-$\mu g/cm^2$	0.0278-$\mu g/cm^2$
11	Molar absorptivity	1,730.77 L/mol/cm	1,265.90 L/mol/cm

Table : 2 Effect of foreign ions

Sr. No.	Interfering ions	Tolerance limit
1	BrO_3^-, Br^-, NO_3^-, IO_3^-, SO_4^-, SO_3^-, CN^-, I^-, Cl^-,ClO_3^-, NO_2^-,	12
2	Tartrate, acetate	10
3	Oxalate , phosphate,	06
4	As(III),W(VI),Mg(II),Mo(VI), Cd(II),	09
5	Al(III), Bi(III), Ce(IV),Ca(II),	10
6	Na^+, Ag^+,K^+	05
7	Co(II), Fe(II), Cu(II), Ni(II), Cr(III)	Interfere strongly

Table-3: Effect of masking agent

Sr. No.	Interfering Ions	Masking Agents
1	Pd(II)	Thiourea
2	Fe(III)	Sodium fluoride
3	Co(II)	Sodium fluoride
4	Ni(II)	DMG
5	EDTA	Boiled with conc.HNO_3
6	CN^-	Boiled with conc.HNO_3 and formaldehyde
7.	Cr(III)	Ammonium acetate
8.	Cu(II)	Sodium sulphate

8. Comparison between reagents

Various reagents were investigated by the earlier researchers for removal of Zr(IV)and Ti(IV). The proposed reagent (HAPED) is found more superior as that of reported regents and are presented in Table 4.

Table 4: Comparison between regents

Sr./Ref. No.	Reagent	Remark
1	Diantipyryl-(p-chloro)-phenylmethane	Beer's range 0-400 μg/25 cm^3
2	Piconaldehyde nicotinoyl hydrazone	Beer's Range 0.02-1.5ppm yellow- coloured complex with M:L ratio as 1:2
3	N,N'-diethylaniline	Require heating At 100ºC
4	Methylene green	Beer's range 0.2-30 cm^3

5	Ethylenebis(triphenyl phosphonium cation	Cr^{+3} interferes
6	5,5'-dithiodi(salicyclo hydroxamic acid	Beer's range 0.3-2.3 tetravalent Fe,Ti, Cu^{+2}, V^{+5} interfere
7	4-(2-pyridylazo) resorcinol	Beer's range < 20µg/50cm³ Fe^{+2},Co^{+2}, Ni^{+2} interfere masked by ascorbic acid
8	Xylenol orange	Beer's range 0.0-16 Fe^{+2}, Zr^{+4},Ti^{+4} interfere masked with F^-

9. Applications

The present method was applied for determination of amount of Zr(IV)and Ti(IV) in various samples of alloys, commercial mixtures, injection vial and tablets. The results obtained were in well agreement with the standard methods shown in Table -5. Every result is the average of independent determinations.

Table 5: Applications

Sr. No.	Sample	Standard method	Present method
1	German alloy	92.0%	91.98%
2	Steel alloy	23.0µg	22.920µg
3	Manganese Ore	37mg	36.85mg
4	Zr(5) + Pd(5)	4.95ppm	4.90ppm
5	Zr(50) + Cd(50) + W(50)	50ppm	49.95ppm
6	Ilmenite ore	80.10%	80.06%
7	Ferro-titanium	40.55%	40.45%
8	Ti(5) + Mn(5)	4.950ppm	4.945ppm
9	Ti(50) + Cd(50) + Cu(50)	50ppm	49.98ppm

and Titanium(IV)

The stability of Zirconiumand Titanium complex is 46hr and 40hr. Represented as in figure:3. It is observed from this figure that a linear calibration curve was obtained in the range of 1-10 ppm Zirconiumand Titanium. In this experiment the results of solvent extraction for removal of Zr(IV) and Ti(IV) by using as (HAPED)organic reagent are presented. Effect of various parameters like pH, absorbance, wavelength and validity of Beer's and Lambert's law. The absorption is observed maximum at wavelength 530 nm and 500nm. The equilibrium is attained within 1 min. The best results of solvent extraction were obtained in aqueous phase at pH 7.8 and 5.6 whereas organic phase containing chloroform as solvent.

1. Effect of pH and absorbance

Chloroform is found to be the most suitable solvent which is carried maximum extraction which is shown in figure 5. 1 cm³ aqueous solution contain 100 ppm Zr(IV) and Ti(IV) at different pH shaking with 2 cm^3 of 0.1% HAPED in chloroform, after separated a two layers measure the absorbance of organic phase at wavelength of 530nm and 500nm and pH of 7.8 and 5.6 respectively which is represented in figure: 6.

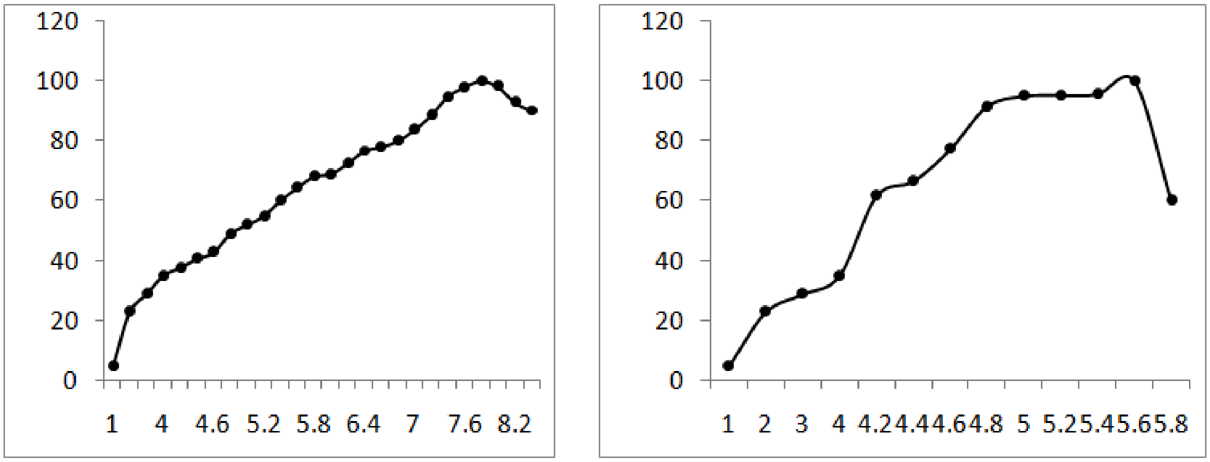


Figure :6- Effect of pH on the extraction of Zr(II) and Ti(IV):HAPED complex

2 Selection of The Solvent

Various solvents were tried to determine the maximum extraction of zirconium and Titanium. Chloroform was found to be most suitable solvent as it showed the maximum extraction. The extraction of zirconium varied from maximum to minimum for the solvent in the order of chloroform > n-butanol >xylene > diethyl ether >carbon Tetrachloride >ethyl Acetate >n-Hexane >nitrobenzene>cyclohexanone >methyl acetate which is shown in figure:7.

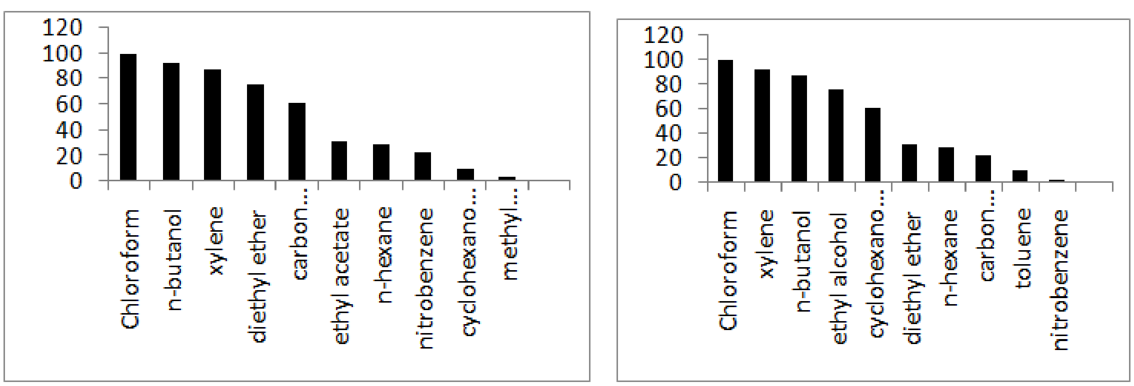


Figure :7 Effect of various solvents on Zr(IV) and Titanium(IV) : HAPED complex

3. Shaking time effect

1-cm^3 aqueous solution contain 100 ppm Zr(IV)and Ti(IV) at pH 7.8 and 5.6 after added 2 cm^3 of 0.1%HAPED in chloroform, shaking for different times (0-60) min. after separating the layers, measuring the absorbance of organic phase at wavelength of 530nm and 500nm.

4 Mole ratio method

Solution of 0.01M HAPED in chloroform used to extract 0.01M Zr(IV) and Ti(IV) from aqueous solution at optimum conditions, also determine absorbance of organic phase at wavelength of 530nm and 500nm respectively against chloroform, figure : 3 indicates that the ratio of Zr(IV) and Ti(IV) to complex was 1:2[Zr^{+4}:(HAPED) and Ti^{4}: (HAPED)].

4. CONCLUSION

The proposed method is more highly sensitive and selective than the reported methods for the extractive spectrophotometric determination of microgram amounts of Zirconium and Titanium. It has been successfully applied to the determination of zirconium and Titanium at trace level in synthetic mixtures and alloys. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference.

DECLARATION

"The facts and the views in the manuscripts are ours and I am totally responsibke for authenticity, validity and originality".I undertake and agree that the manuscripts submitted to your journal have not been published elsewhere and have not been simultaneously submitted to other journals. I also declare that manuscript is my original work and we have not copied from anywhere else. There is no plagerism in my manuscripts.

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