

Selective Extraction of Zirconium from Various Samples and Subsequent Spectrophotometric Determination with Eriochrome Cyanine R Reagent

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ABSTRACT

A sensitive and selective spectrophotometric method for the determination of zirconium(IV) in various samples has been developed. In this method trioctylphosphine oxide (TOPO) is used for the extraction of zirconium. The colour of the complex is developed in the organic phase by the addition of eriochrome cyanine R reagent (ECR) and ethanol as a diluent. The calibration plot is linear in the concentration range 0.08–10 $\mu\text{g ml}^{-1}$ with a molar absorptivity (ϵ) of $2.0 \times 10^4 \text{ l.mol}^{-1} \text{ cm}^{-1}$ at 564 nm. The stoichiometric composition of the chelate is 1:2 (Zr : ECR). The extraction of zirconium (IV) was carried out in the presence of various ions to ascertain the tolerance limit of individual ions. The proposed method was successfully used for the determination of zirconium in various samples such as, natural waters and ores .

/ (10^{-0.08})

(6.2)

/ (10⁴ x2)

. 564
. ² / (0.0045)

INTRODUCTION

Zirconium is widely distributed in nature. The principal ores are zircon ($ZrO_2 \cdot SiO_2$) and elpidite ($Na_2ZrSi_6O_{15} \cdot 3H_2O$). Many different methods, such as: ion selective electrode (Arid, 2008), inductively coupled plasma isotope dilution-mass spectrometry (ICP-IDMS) (Dimer and Heumann, 1999), high performance liquid chromatography (HPLC) (Xin and Xianzhong, 2004), stripping voltammetry (Domenech-Carbo *et al.*, 2004) (Li *et al.*, 2007), and atomic absorption spectroscopy (Chakraborty and Das, 1989), have been used for the determination of zirconium in aqueous solution, polyolefins, steel, minerals and ceramic materials and granite rocks, respectively. In most of these methods, ion exchange, solvent extraction, or expensive and special equipments are required. Others are time consuming, not selective and suffer from property of Zr to form refractory oxides and carbides resulting in a poor sensitivity. A large number of spectrophotometric methods have been used for assay of zirconium in rocks, water and minerals, mineral water, industrial water, zirconium and magnesium alloys, using arsenazo III (Changfa, 1988), alizarin-red S (Hassanien 2005), 2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone (Sivaramaiah *et al.*, 2003), 3,4-dihydroxyazobenzene (Vilkova and Invanov, 1989), and 1-(2-pyridylazo)-2-naphthol (PAN) (Ysumaso and Takehiro, 1981) as reagents, respectively. In some of these methods, in spite of using a separation step to improve the selectivity, interferences from many cations and anions were still observed. Others suffer from low sensitivity, are time consuming and no applications as well as organic solvents are required. ECR reagent has attracted much attention as a spectrophotometric reagent because of its high sensitivity. It has been applied to the spectrophotometric determination of many metal ions such as, Th, Fe(III), Mg, Ca, Ga, Be and rare earth elements (Jarosz and Malat, 1988). In order to increase the selectivity, a reliable separation technique like solvent extraction is necessary before the spectrophotometric determination of zirconium by ECR. Literature survey showed that various solvent extraction methods for the separation and pre-concentration of zirconium are available. Different reagents such as, arsine oxides (Ejaz, 1976), mesityl oxide (Mudshingikar and Shinde, 1983), 2-hydroxy-5-nonylaceto-phenone-oxime (LIX 84-IC) (Reddy *et al.*, 2004), 2-ethylhexyl phosphoric acid mono-2-ethyl-hexyl ester (PC-88A) (Reddy *et al.*, 2004), Cyanex 923 (Gupta *et al.*, 2005) and organophosphorus compounds (Minczewski *et al.*, 1982) have been reported for extraction of zirconium. However, most of the existing methods suffer from limitations, such as, longer extraction time, toxicity, hydrolysis, incomplete extraction or difficulty in the synthesis of arsine oxides. Organophosphorus reagents of the type tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) are still the best extractants for zirconium due to their high dipole moment and the presence of the electronegative ($-P=O$) oxygen atom with donor properties (Mohammed, 1995), (Minczewski *et al.*, 1982). TOPO was preferred over TBP due to its extraction efficiency, stability even towards radiation and enhanced selectivity. TOPO solution has been used to extract many elements, usually, metals in their highest oxidation states (Mohammed, 1995). The extraction of zirconium from different acidic media by TOPO solution in cyclohexane or acetophenone and subsequent spectrophotometric determination with PAN reagents using methanol as a solvent has been investigated (Ysumaso and Takehiro, 1981).

In the present work, a detailed investigation of the solvent extraction of zirconium (IV) with TOPO in cyclohexane solution has been developed and the zirconium, thus, separated was determined spectrophotometrically with ECR reagent in various samples.

EXPERIMENTAL

Apparatus

The absorption spectra were recorded on a Shimadzu (Model-160) double-beam UV/VIS Spectrophotometer with 1.0-cm matched quartz cells. Phillips PW 9421 pH meter was used for all pH measurements.

Atomic absorption spectrophotometer Shimadzu (AA-670) graphic printer PR-4 was used for all sample ores measurements.

Reagents

All chemicals used are analytical-reagent grade and all standard solutions are prepared using double distilled water.

Stock solution (1000 $\mu\text{g/ml}$) of Zr(IV). It was prepared by dissolving 0.3531 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Fluka) in 100 ml distilled water using a volumetric flask. Working solution of zirconium (IV) was prepared by appropriate dilution of the stock solution with distilled water.

ECR ($2.0 \times 10^{-3}\text{M}$) solution. It was prepared by dissolving 0.0536 g of ECR reagent trisodium salt (Fluka) in distilled water and the solution was diluted to 100 ml in a volumetric flask. The solution was transferred to a brown bottle and is stable for only 48 hrs.

TOPO (0.1M) solution. It was prepared by dissolving 19.3 g of TOPO (Fluka) in 500 ml cyclohexane using a volumetric flask.

Triethanolamine-HCl buffer solution (pH 6.2). It was prepared by mixing a required volume of 0.1M HCl with 700 ml of solution containing 7.45 g of triethanolamine and the pH was adjusted to 6.2 (using pH meter) and the volume was diluted to 1 L with distilled water.

Ascorbic acid (5%) solution. It was freshly prepared by dissolving 2.5 g of ascorbic acid (BDH) in distilled water and the solution was diluted to 50 ml in a volumetric flask. The solution was transferred to a brown bottle.

General procedure

An aliquot of solution containing 10-1250 μg of zirconium was transferred to a 50-ml separatory funnel followed by the addition of 8 ml of 4 M HNO_3 and 1ml of 5% freshly prepared ascorbic acid, and the volume was completed to 20 ml with distilled water. The mixture was shaken with 5 ml of 0.1M solution of TOPO in cyclohexane for 3 min. After separating the two phases, 1 ml of the organic phase containing zirconium was pipetted to a 25-ml beaker followed by the addition of 1ml of ECR reagent, 1ml of triethanolamine-HCl buffer solution and enough volume of 0.1M NaOH solution to adjust the pH of the mixture to 6.2 (using pH meter). The mixture was transferred to a 25-ml volumetric flask and diluted to the mark with ethanol and allowed to stand for a further 10 min, then the absorbance was measured at 564nm against the corresponding reagent blank.

RESULTS AND DISCUSSION

Preliminary investigation

The colouring reaction between 40 μ g zirconium(IV), 2 ml of 2×10^{-3} M ECR reagent and ethanol in the apparent PH range 3.5 - 10.5 was investigated (Fig.1). pH 6.2 was considered the optimum because of the high sensitivity and good colour contrast. Therefore, different buffers of pH 6.2 were prepared and their efficiency was also tested in terms of the added amount. A 2 ml of triethanolamine-HCl buffer solution of pH 6.2 at maximum absorption 564nm were selected for the subsequent experiments. It was found that the method without extraction had weaker selectivity to make the determination of zirconium in matrix of other ions possible. Therefore, solvent extraction step was incorporated in the procedure to make the method more analytically useful .

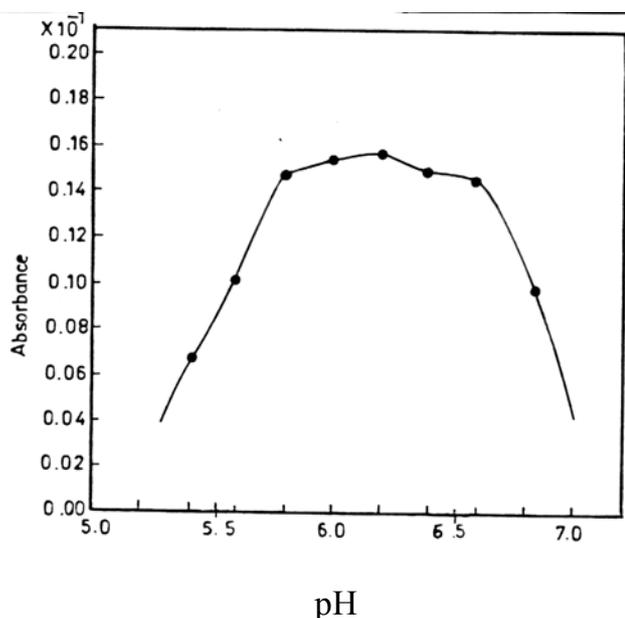


Fig 1: Effect of apparent pH on the absorption of Zr-ECR complex

Effect of TOPO concentration and aqueous acidity

The extraction of 60 μ g of zirconium (IV) was carried out with different concentrations of TOPO in cyclohexane (0.05-0.2)M over the acidity range of 1-8 M HNO₃ by keeping the aqueous to organic volume ratio 4 :1. The results showed that 5 ml of 0.1M TOPO in cyclohexane was needed for quantitative extraction of zirconium(IV) in a single 1 min equilibrium step from 4M HNO₃ (Fig.2). The species extracted from nitric acid by TOPO was found to be Zr(NO₃)₄.3TOPO (Mudshingikar *et al.*, 1983) . Although the extraction was quantitative in hydrochloric acid, but a higher concentration of acid and a greater equilibrium time was required. Extraction was incomplete in perchloric acid due to emulsion formation, while low extractability was obtained in sulphuric acid, (due to the formation of soluble complexes with sulphate anions). Therefore, 4 M nitric acid was recommended and 8 ml of this acid was used for further studies .

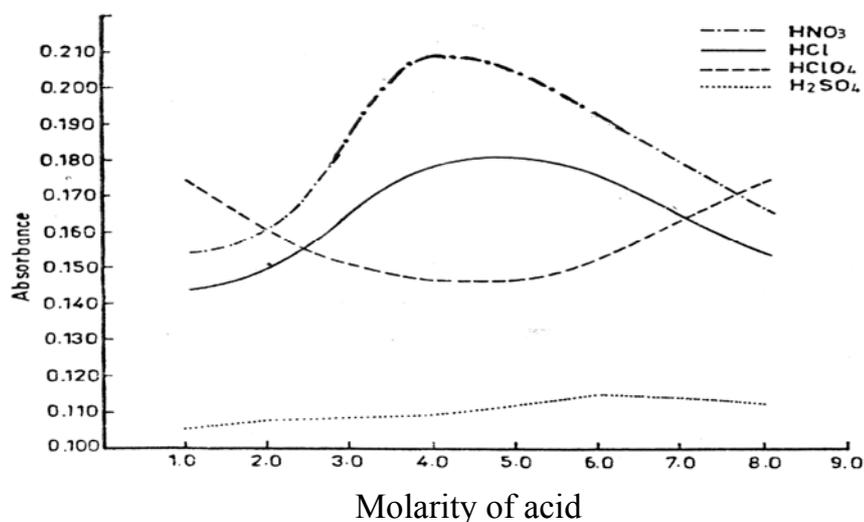


Fig 2: Extraction of Zr(IV) with TOPO in cyclohexane as a function of acid concentration

Effect of ascorbic acid

The high valency states of metal ions extractable by (TOPO) can be reduced to the lower ones, by addition of ascorbic acid, which are not capable to extract or have low extractability such as, Fe^{3+} , Ce^{4+} , V^{5+} . The results showed that about 1-5 ml of 5% ascorbic acid give a higher extractability. Therefore, 1ml of ascorbic acid solution was selected for subsequent experiments.

Effect of volume ratio and period of equilibrium

The volume ratio of aqueous phase to organic phase was examined with the variation of the shaking time from 1 to 10 min. The results showed that the extraction of zirconium (IV) was quantitative when the aqueous to organic volume ratio was 4:1 and 3 min of equilibration time.

Effect of the amount of buffer solution on absorbance

The amount of pH 6.2 triethanolamine-HCl buffer solution which gave maximum absorbance was tested. It was found that a 1 ml volume of the buffer solution gave optimum sensitivity.

Effect of reagent amount and stability of complex

Under the obtained optimum conditions and using 1.0 ml of 2×10^{-3} M ECR solution, the formation of the coloured complex reaches equilibrium after 10 min.

Final absorption spectra

Under the above established optimized conditions, zirconium ion form complex with ECR reagent at pH 6.2 (Fig 3). The coloured complex exhibits maximum absorption at 564 nm which is maintained for subsequent work.

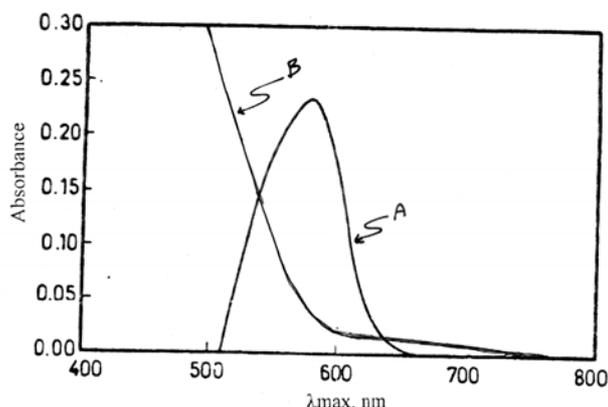


Fig 3: Absorption spectra of Zr(IV) – ECR (A) against reagent plank, (B) blank against distilled water.

Calibration graph and reproducibility

The calibration graph was linear for 2-250 μg of zirconium /25 ml (i.e 0.08 – 10 ppm). The molar absorptivity (ϵ) and the Sandell sensitivity were $2.0 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and $0.0045 \mu\text{g cm}^{-2}$ of zirconium, respectively. Job's continuous variations and the molar – ratio methods were applied to ascertain the stoichiometric composition of the complex. Zr - ECR (1:2) complex was indicated by both methods. The reproducibility for 40 μg Zr(IV) (five replicates) was 1.78% (R.S.D)

Effect of foreign ions

Zirconium (IV) was extracted in the presence of a large number of foreign ions Individual tolerance limit of foreign ions on the determination of 100 μg of zirconium (IV) was determined with an error of $\pm 2\%$ in the recovery of zirconium (Table 1). It was observed that the recommended method was free from interferences from a large number of transition, non-transition metal ions and anions.

Table 1: Individual tolerance limit of foreign ions on the determination of 100 μg of Zr

Ratio of ions Zr (IV) : ion	Cation	Anion
1 : 25	$\text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$	$\text{Cl}^-, \text{Br}^-, \text{NO}_3^-$
1 : 15	$\text{Cd}^{2+}, \text{Co}^{2+}, \text{Cr}^{3+}, \text{Mn}^{2+},$ $\text{Zn}^{2+}, \text{Pb}^{2+}$	
1 : 10	$\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ba}^{2+}, \text{Ni}^{2+},$ $\text{Bi}^{3+}, \text{Cr}^{6+}, \text{V}^{5+}, \text{La}^{3+}$	$\text{SO}_4^{2-},$ $\text{IO}_4^-, \text{SO}_3^{2-}, \text{PO}_4^{3-}$
1 : 3	$\text{Th}^{4+}, \text{UO}_2^{2+}$	
1 : 0.5	Al^{3+}	

APPLICATION

Determination of zirconium in natural waters

An aliquots of 5-15 ml of the sample solution containing three different amounts of zirconium (IV) were taken into 50 ml separatory funnel and the zirconium content was analyzed by the recommended procedure and the results are given in Table 2, indicated that the present method for the determination of Zr (IV) can be used with satisfactory results .

Table 2: Determination of zirconium in natural water.

Sample	volume of sample, ml	zirconium added , μg	recovery [#] , %	
Tap water	5	20	105.0	
		100	101.0	
		150	103.3	
	10	20	92.5	
		100	102.0	
		150	96.6	
15	20	97.5		
	150	97.3		
	River water*	5	20	95.0
		100	100	105.0
			150	98.6
	10		20	92.5
150		100	101.3	
		150	101.3	
	15	20	105.0	
100		101.0		
150		101.3		
Sea water**		5	20	100.0
		100	100	102.0
			150	102.0
10	20		97.5	
	150	150	98.6	
		15	20	90.0
100			100	96.7
	150		150	96.6

Average of three determinations.

**Synthetic sea water was prepared according to the formula given in (Henriksen, 1965)

* Tigris river .

Determination of zirconium in ores

The proposed method was successfully applied to the assay of zirconium in clay and iron stones .In this method, 1g of finely ground sample was weighed and mixed with 5 g of Na_2CO_3 in a porcelain crucible. The mixtures were fused at 1000 C° for 30 min. After fusion

process, 1ml of HCl was added and heated until most of the acid has evaporated. The residues were then dissolved in 5 ml HCl (1+1). If the solutions were not clear they were filtered and the residues on the filters were carefully washed. The filtrates and the washings were collected in a 25-ml beaker and the pH of the final solutions were adjusted to 6.2 (using pH meter). The mixtures were then transferred to 100-ml calibrated flasks and diluted to the mark with distilled water. An aliquot (1-2 ml) of the dilute solution was pipetted into 50-ml separatory funnels and the zirconium contents were determined by the recommended procedure. The results are shown in Table 3 compared with another reported method.

Table 3: Determination of zirconium in ores

Sample number	Zirconium content* , ppm		
	present method	XO ^a (Marczenko, 1976)	AAS ^b
IA ^c	2.9	2.8	2.6
IIA ^c	3.3	3.2	3.2
IIIA ^c	3.6	3.2	3.5
IB ^d	2.4	2.0	2.3

*Average of three determinations

a. by spectrophotometric method using xylenol orange as a reagent .

b. by AAS technique .

c. Clay stone (Al-Amege zone) west of Iraq .

d. Iron stone (Al-Husyniatt zone)

In order to test the result for the existence of a systematic error for the present method, " t " test for assay of zirconium in natural waters and ore sample was used. The t_{exp} was calculated as described in (Christian, 2004) and compared with flame atomic absorption spectrometric method. As can be seen from the results, the values of t_{exp} are less than 2.776 (" t " test from table) at 95% confidence for four degrees of freedom indicating that the present method has good validity (table 4).

Table 4: The value of " t " test of natural waters and ore sample

Sample	tap water	river water	sea water	IA ^c
t_{exp}	0.884	1.825	0.571	0.542

Comparison of the method

Table 5 shows the comparison of spectrophotometric methods for Zr(IV) determination, based on the formation of complexes with ECR reagent.

Table 5: Comparison of the method

Parameters	Method	
	This work	ECR (Mather, 1971)
pH	6.2	5.0-5.2
λ_{\max} , nm	564	590
Beer's law range, ppm	0.08-10	-----
Molar absorbtivity, $l.mol^{-1}.cm^{-1}$	2×10^4	6×10^4
Time for colour development, sec,	10	15
Sandell index, $\mu g.cm^{-2}$	0.0045	0.0015
Recovery, %	99.4 – 106.2	-----
RSD, %	1.09 – 2.25	-----
Stability period, hr	>1hr.	2hrs.
Stability constant of complex, $l^2.mol^{-2}$	4.16×10^6	-----
Surfactant	-----	polycyclic ketoamine
Applications	applicable to natural water (tap, river and sea waters) and ores	applicable to alloy steels

CONCLUSION

A selective and sensitive spectrophotometric method for the determination of zirconium in various samples has been carried out. TOPO was used for the extraction of zirconium, a colour was developed in the organic phase by the addition of ECR reagent. The method was characterized by simplicity and the wide range of applications.

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