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Spectrophotometric determination of zirconium (IV) and hafnium (IV) with pyrazolo (1, 5-a) quinazolin-6-one derivative reagent

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ABSTRACT

The present work considers a new reagent 2-amino-3-(4-bromo phenyl azo)-8,9 dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one (BrPhPQ) for the selective determination of zirconium and hafnium ions in aqueous solution. A complete study is made to ascertain the (BrPh-PQ) for quantitative determination of Hf ions in presence of Zr species. The reagent gave a stable yellow colored complex with both metal ions under the same conditions of pH but the Hf-complex was not formed at pH 3.2-4.7 range. The complex had an absorption maximum at 368 nm and followed Beer's law in the concentration range (0.005-1) $\mu\text{g/ml}$. The molar absorptivities of aqueous Zr and Hf complexes were 1.68×10^5 and $2.51 \times 10^5 \text{ l.mol}^{-1}.\text{cm}^{-1}$ respectively. The method was applied for direct determination of Hf (IV) and Zr (IV) in zircon mineral. Results of analysis using the suggested procedures were in good agreement with the other similar published data elsewhere.

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KEYWORDS

2-amino-3-(4-bromo phenylazo)-8,9 dihydro-7H-pyrazolo[1,5-a] quinazolin -6-one;
Determination;
Zirconium;
Hafnium;
Spectrophotometric.

INTRODUCTION

Numerous reagents had been proposed for spectrophotometric determination of Zr (IV) in particular, the metallochromic indicators^[1-7], however, Hf (IV) interfered seriously. Therefore, it was little bet difficult to find a specific analytical reagent for each one. The principal of these techniques depended mainly on the existence of several differential methods, based on differences between Zr and Hf complexes or the presence of specific masking agents^[8-10]. A survey of the literature showed that a limited number of specific chromogenic reagents had been used for determination of Hf (IV) in the presence of Zr (IV)^[11]. The most common methods for the later determinations of elements were reported by Cheng and Challis^[12]. Cheng's method for

determination of Hf (IV) is based on the use of hydrogen peroxide to mask Zr (IV). Also, simultaneous determination of both metal ions in high temperature alloys was introduced by Dulski^[13]. The reactions of Zr (IV) and Hf (IV) species with 4-(2-pyridylazo)-2-naphtholenol (PAN), arsenazo III, 4-(2-pyridylazo) resorcinol (PAR), 2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone and salicyl fluorone were reported^[14-18]. The 2,2',3,4-tetrahydroxy-3'-sulpho-5'-carboxazobenzene reagent and Janus green dye were also proposed^[19,20]. Actually, most of these methods suffer from low sensitivity and selectivity.

A series of synthesized reagents were tried for availability of Zr (IV) and Hf (IV) determination. This work presents a new synthesized reagent to be used for direct determination of Zr (IV) and Hf (IV) in aqueous

solution. To develop the reagent, the parameters (pH, absorption spectra, concentration of dye, etc...) that affect Zr (IV) and Hf (IV) analysis have been investigated to provide optimum conditions for their determinations.

EXPERIMENTAL

Reagents and solutions

BrPh-PQ solution. An accurate weight of 2-amino-3-(4-bromo phenyl azo)-8,9 dihydro-7H-pyrazolo (1,5-a) quinazolin 6-one was dissolved in 100 ml of ethanol/N,N dimethyl formamide (DMF)^[21].

Zirconium (IV) oxychloride octahydrate powder ($ZrOCl_2 \cdot 8H_2O$, 99.5%, Riedel de Haën), hafnium oxide powder HfO_2 (98.0%, Aldrich), sodium hydroxide pellets (97%, Sigma-Aldrich), sulphuric acid (18 M, 98%), hydrochloric acid (12 M, 36.5%) and sodium pyrosulfate powder (99%, Fischer) used, were of analytical reagent grades.

Analytical procedure

Zirconium solution. Stock solution of 1000 $\mu\text{g/ml}$ Zr (IV) was prepared by direct dissolution of 0.353 gm zirconium oxy chloride $ZrOCl_2 \cdot 8H_2O$ (Riedel de Haen) in 100 ml 2M HCl.

Hafnium solution. The 1000 $\mu\text{g/ml}$ Hf (IV) stock solution was prepared by fusing 0.118 gm HfO_2 (Aldrich) with 2 gm sodium pyrosulfate then dissolved in 10 ml diluted H_2SO_4 (1:1) and completed to 100 ml with distilled water.

Working solutions of Zr (IV) and Hf (IV) were prepared and used for analytical experiments.

Zircon sample preparation. A 0.05 g of zircon sample (99.5%) supplied from Nuclear Materials Authority, was mixed, fused and heated with 1.0 g of sodium hydroxide for 30 minutes. The digested sample was leached and dissolved in 30 ml HCl acid solution (1:1) while heating then mixed and diluted with double distilled water up to 100 ml^[21].

Synthesis of organic compound (BrPhPQ)

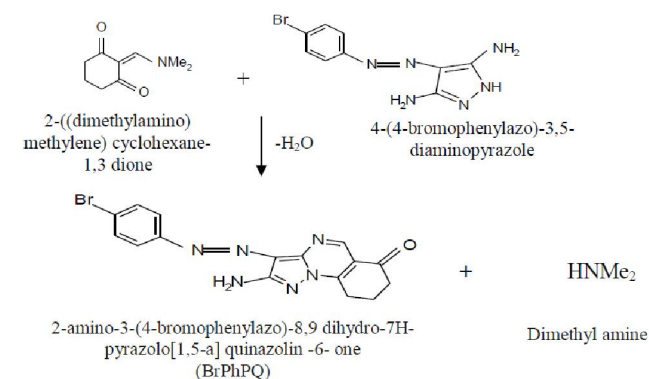
For this purpose, one β -diketone namely; 2-((dimethyl amino) methylene) cyclohexane-1,3 dione in pyridine, (10 m mol) was selected as starting material. To the latter an appropriate amino pyrazolo derivative (10

m mol) was added and refluxed for 30 min. The solid product was filtered off, washed with ethanol and recrystallized in dimethyl formamide (DMF) to afford the pyrazolo (1,5-a) quinazolin-6-one derivative in 96% yield, mp. > 300 °C (ethanol /DMF)^[22]. The reagent has yellow color, stable at room temperature and soluble in organic solvents. Constancy of melting point and I.R spectrum of the synthesized reagent proved that the stability of the reagent. The spectral data of the synthesized compound is listed below, and illustrated in TABLE 1 and Figure 1-3.

TABLE 1 : Spectral data of synthesized compound (BrPhPQ).

Type	Analysis
IR (KBr) $\gamma_{\text{max}}/\text{cm}^{-1}$	3425, 3271 (NH ₂), 1682 (C=O), 620 (C=N), 1543 (C=N)
¹ H NMR (DMSO-d ₆)	δ 2.22(t, 2H, CH ₂), 2.65(t, 2H, CH ₂), 3.30(m, 2H, CH ₂), 7.40 (S, 2H, NH ₂), 7.67 – 7.83(m, 4H, ArH), 8.85 (S, 1H, CH)
MS (m/z)	386 (M+1), 385 (M ⁺), 278, 229, 145, 107, 67
Analysis of imperial formula	Calculated
$C_{16}H_{13}BrN_6O$ (385.22)	C, 49.89; H, 3.40; Br, 20.74; N 21.82 %
	Found
	C, 49.91; H, 3.43; Br, 20.70; N 21.85 %

The reaction of 2-amino-3-(4-bromo phenylazo)-8,9 dihydro-7H- pyrazolo [1,5 -a] quinazolin-6-one is shown in the following Scheme 1.



Scheme 1

Color development and spectrophotometry

To 25 ml flask containing an aliquot of Zr (IV) and Hf (IV) at solution pH 6, 1.25 ml of 0.025% BrPhPQ solution was added, mixed and then diluted to the mark with double distilled water. In the required cases, the pH of the aqueous solution was adjusted to the desired value using 2M NaOH and 2M HCl solutions. The re-

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action was instantaneous and maximum absorbance was attained after 15 min. The absorbance was measured

at 368 nm in 1.0 cm cell against water reagent blank as reference.

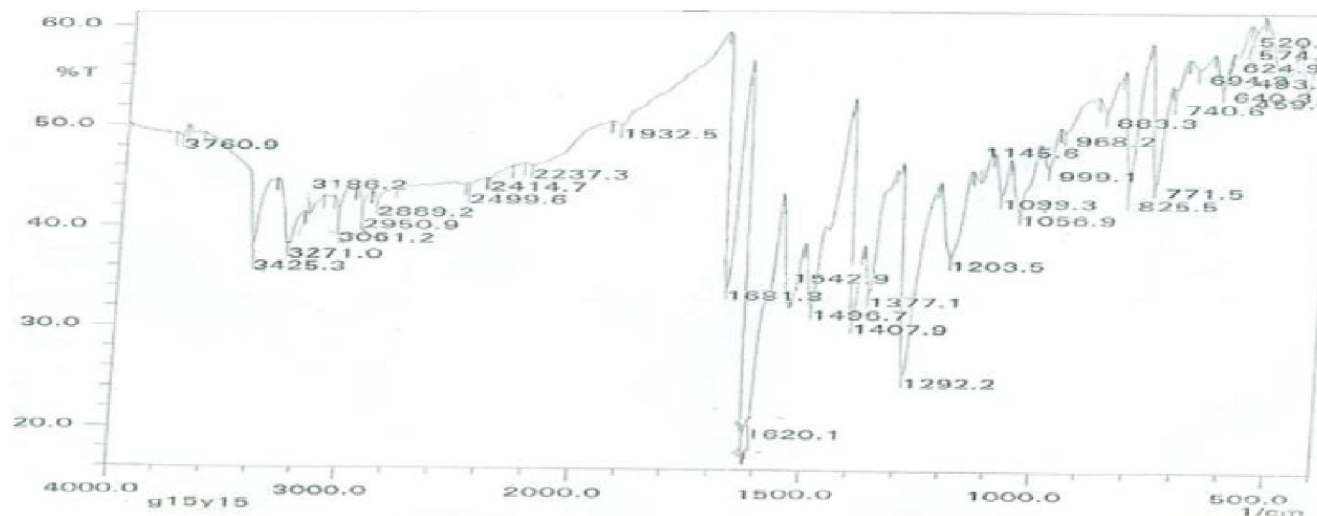


Figure 1 : IR spectra of BrPhPQ reagent powder.

Element analysis

Spectrophotometric analysis of Zr and Hf elements were performed using spectrophotometer, Unicam UV2-100. The concentrations of other elements including (silica, total iron, etc.) were determined using the standard methods of analyses^[23].

IR spectra of the reagent and prepared complexes were recorded in potassium bromide disks using a Pye Unicam SP 3300 and Shimadzu FTIR 8101 PC IR-spectrophotometers. NMR and Mass spectra were recorded using Varian Mercury VXR-300 NMR and Shimadzu GCMS-QP 1000 EX mass spectrometers respectively at accurate analysis lab., Cairo University.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of BrPhPQ ligand and its (Zr (IV) and Hf (IV)) complexes were made against reagent blank solution prepared in the same way as the analytical solution. It showed well defined peak at 368 nm. The absorption spectrum of the blank, the Zr-complex and Hf-complex at pH 6 is illustrated in Figure 4.

Effect of variables

(a) Effect of pH

The effect of pH on the color development of BrPhPQ of Zr and Hf complexes was investigated at

pH (1-12) values. Zr ions reacted quantitatively in the pH range 4-7 as shown in Figure 5, however, Hf chelate was not formed over the pH range 3.2-4.7. This behavior can be explained on the bases that the chemistry of zirconium and hafnium species is closely connected to their capability to form polymeric species under acidic condition^[24]. Zamora and Martins stated that hafnium presents a higher tendency to polymerise in solutions forming polymeric species that hinder its complexation^[8]. Therefore, the acidity should be carefully controlled to determine both metal ions.

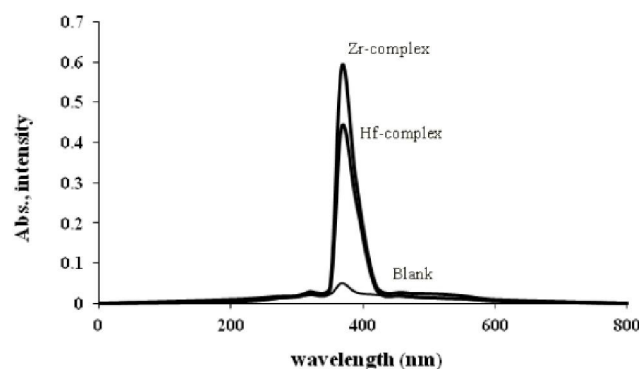


Figure 2 : Absorption spectra of Zr-BrPhPQ.

(b) Effect of BrPhPQ concentration

At concentration (0.3 $\mu\text{g/ml}$) of the studied cations species, the absorbance of complex initially increased rapidly with increase of the BrPhPQ ligand concentration, then leveled off at the maximum concentration of 0.025% BrPh-PQ in ethanol/N,N dimethyl formamide,

Figure 6. Thus, 0.025% is considered as optimum BrPhPQ concentration and was selected for subsequent experiments.

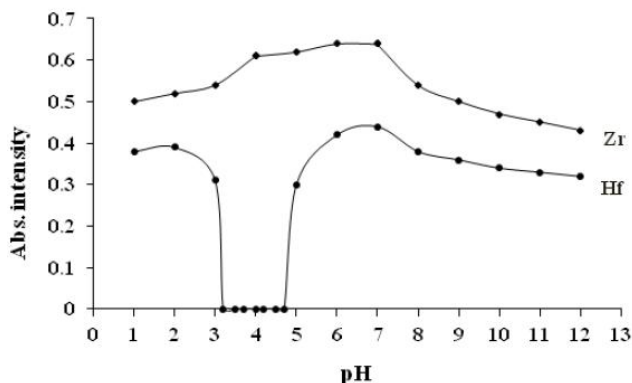


Figure 3 : Effect of pH on the formation of Zr and Hf complexes.

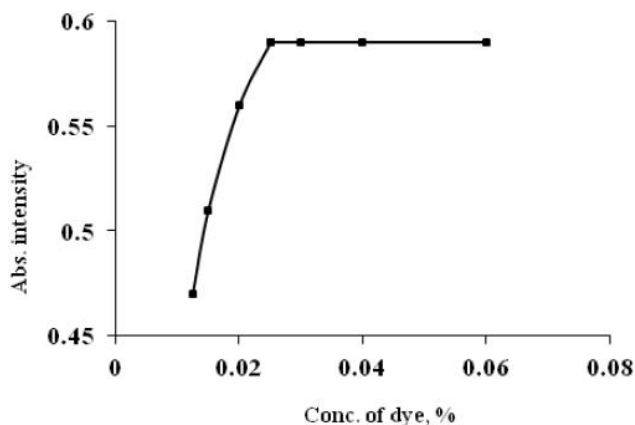


Figure 4 : Effect of BrPhPQ concentration on color development.

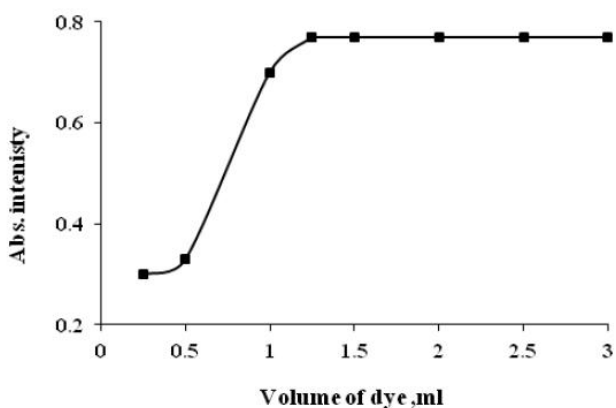


Figure 5 : Effect of volume of BrPh-PQ on complex formation.

(c) Effect of volume of BrPhPQ

The obtained data indicated that 1.25 ml of 0.025% BrPhPQ solution was adequate for obtaining maximum absorbance of 0.3 µg/ml of Zr or Hf ions studied in 25

ml flask, Figure 7.

(d) Effect of time

This effect was studied at various time periods ranging from 5 to 210 min. The obtained results, Figure 8, proved that the absorbance of Zr chelate occurred within few minutes where the absorbance intensities were gradually increased by increasing the standing time and reached the constant values after 15 min. The absorbance of this complex was constant over a time period extended to 180 min. After the latter time, the complex was gradually decomposed.

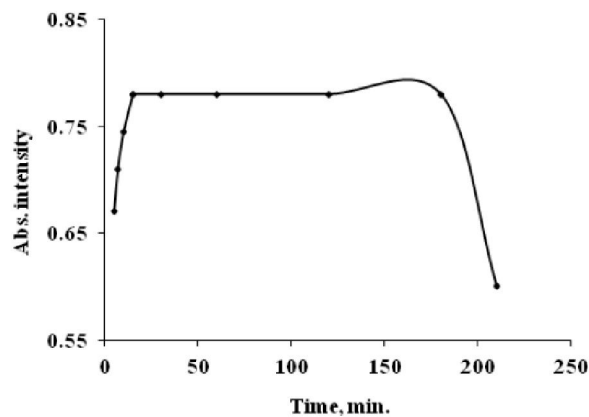


Figure 6 : Effect of time on color development of the formed Zr-complex.

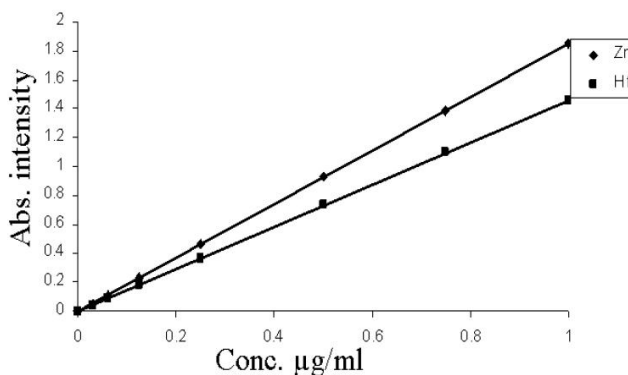


Figure 7 : Calibration curves of Zr and Hf with synthesized reagent BrphPQ.

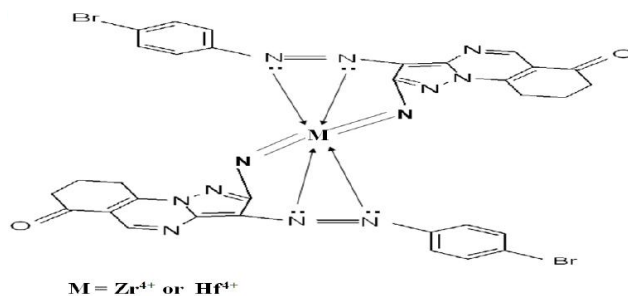


Figure 8 : Structure of complex.

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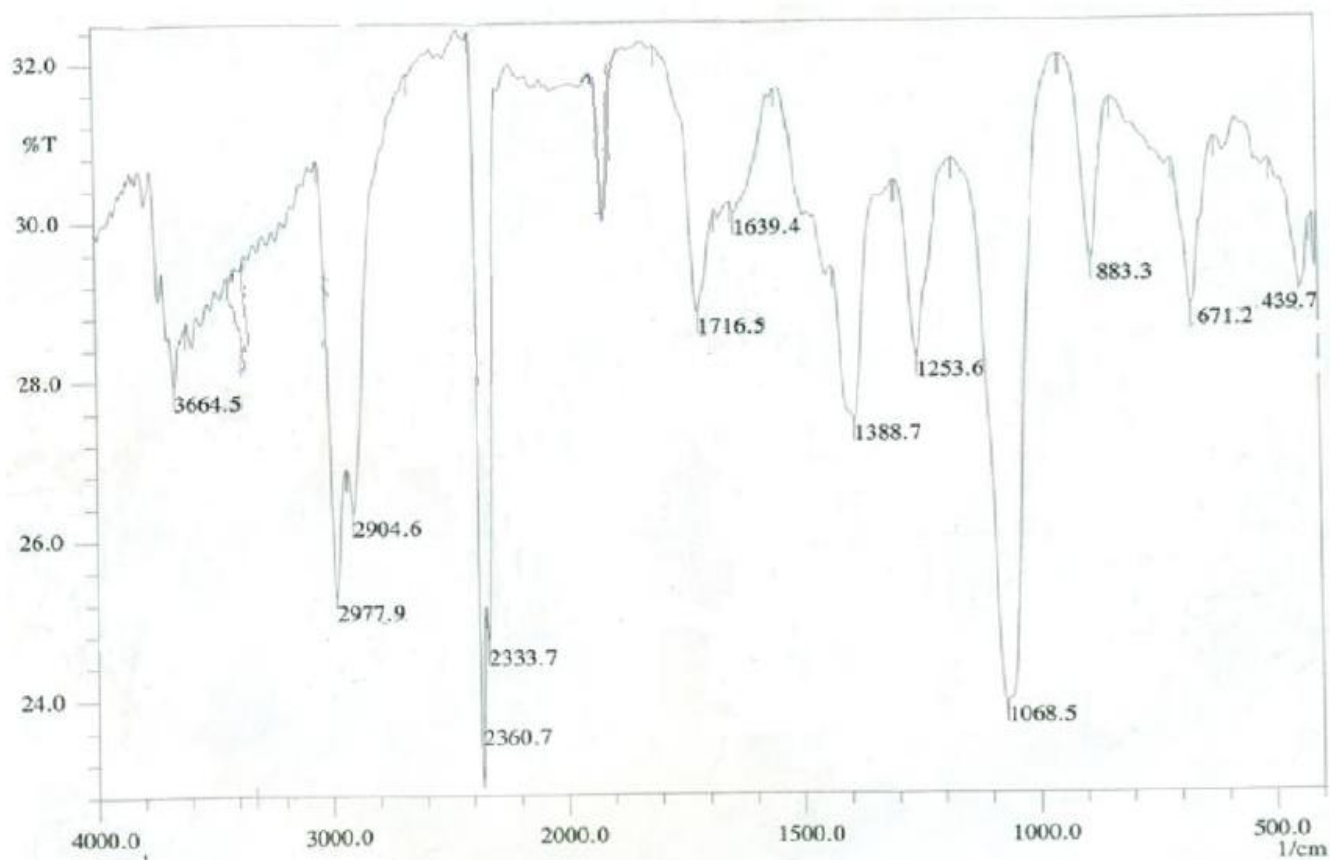


Figure 9 : IR analysis of synthetic compound in ethanol/DMF.

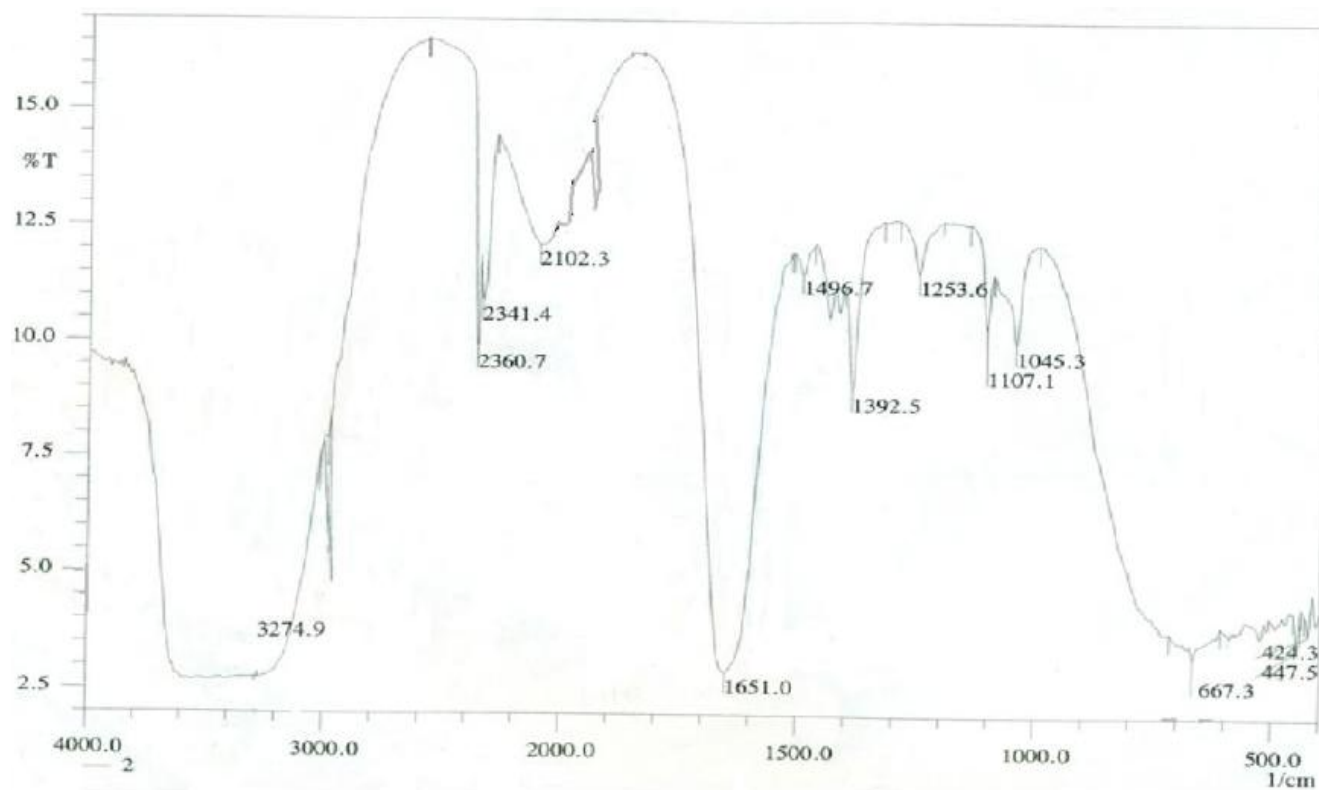


Figure 10 : IR analysis of Zr-(BrPhPQ) complex at pH 6.

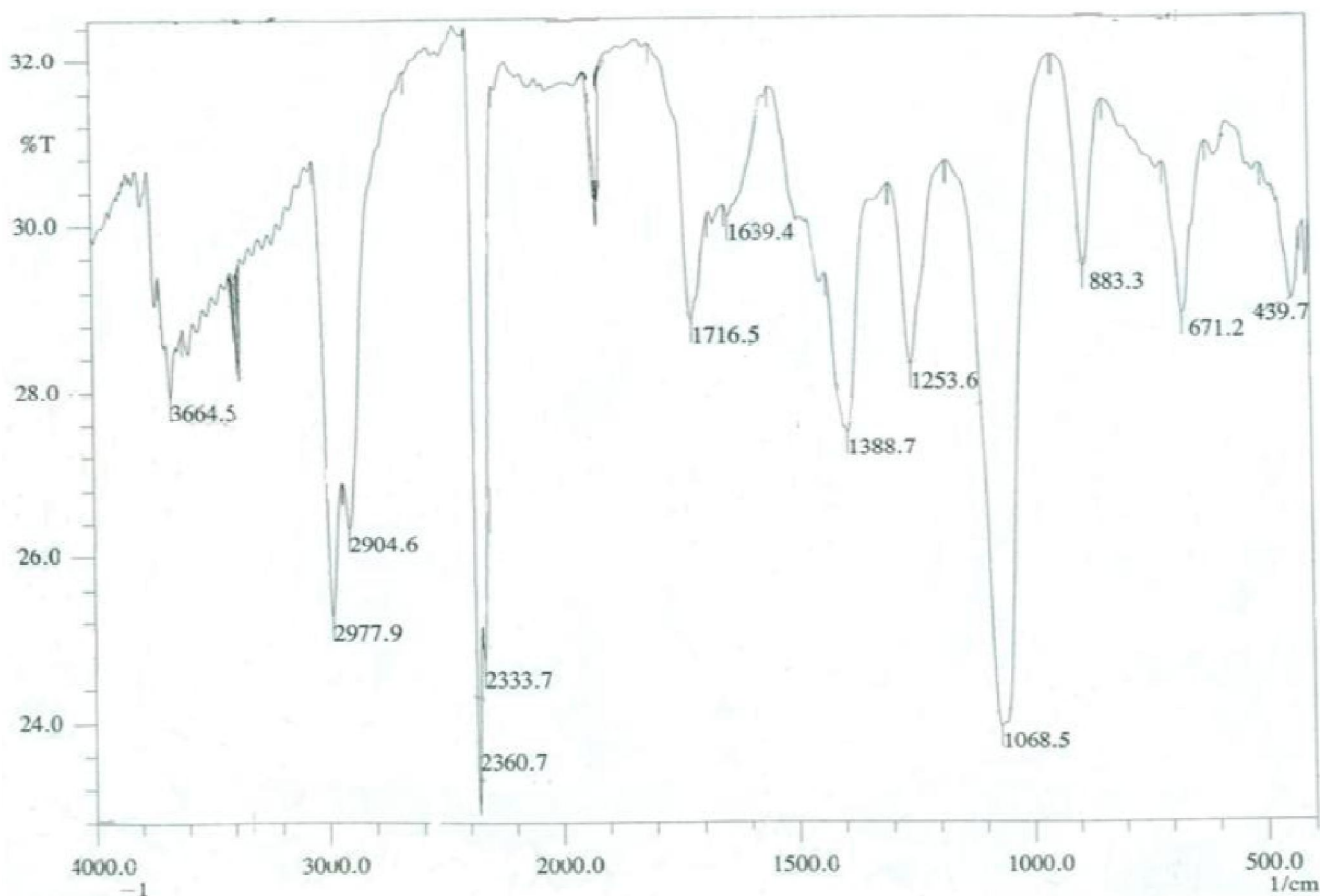


Figure 11 : IR analysis of Hf – (BrPhPQ) complex at pH4.

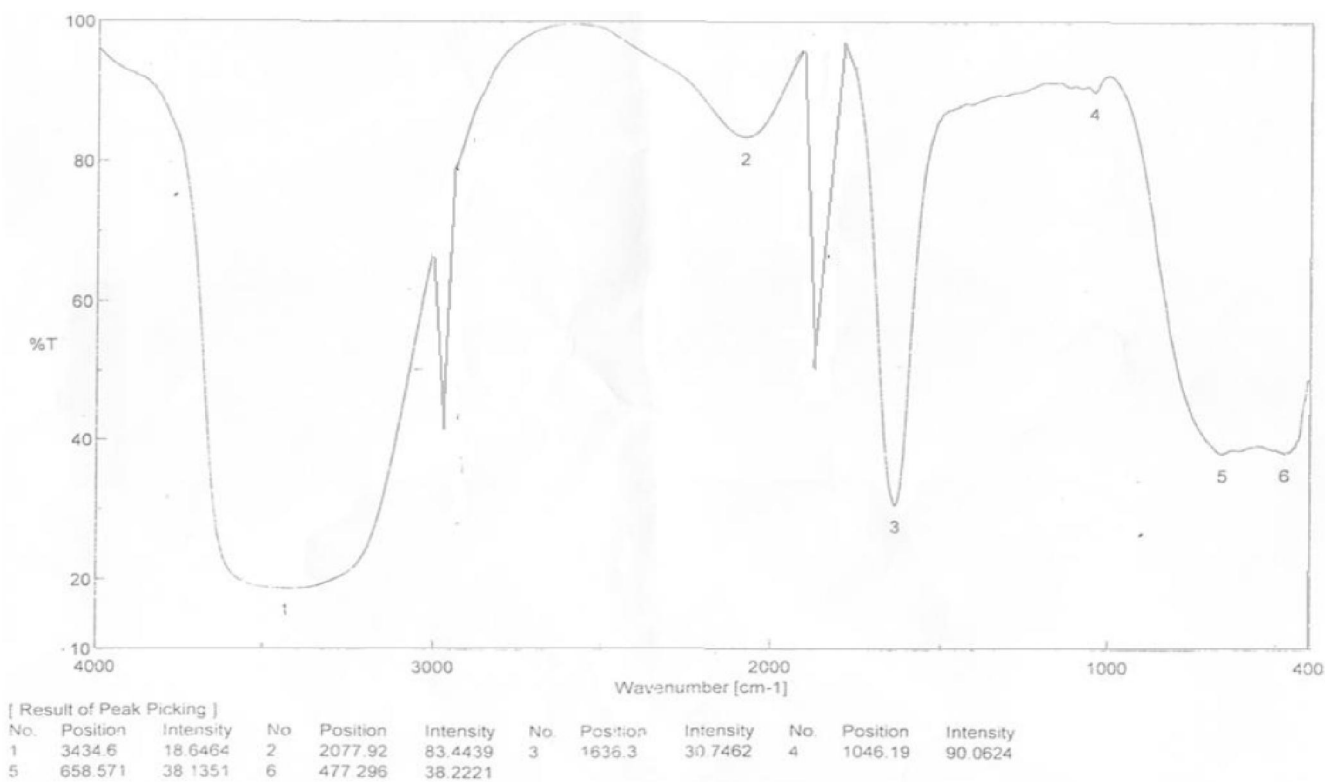


Figure 12 : IR analysis of Hf – (BrPhPQ) complex at pH6.

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(e) Beer's law

Under the optimum conditions, the constructed calibration curves, Figure 9 were linear in the concentration range 0.005-1 $\mu\text{g/ml}$, with correlation coefficient 0.999. The standard deviations obtained from ten measurements of 0.25 $\mu\text{g/ml}$ Zr standard solution was 0.06. Job's method^[25] of continuous variation and the molar ratio method were applied to ascertain the stoichiometric composition of the complex. A Zr:BrPhPQ (1:2) complex indicated by molar ratio. The structure of the Zr or Hf complex was illustrated in Figure 10.

(f) Analysis of synthetic mixtures

As previously mentioned, both (Zr (IV) and Hf (IV)) complexes absorbed appreciably at pH 6 while in the range pH 3.2-4.7 only Zr-complex was absorbed. Thus if the color of a mixture of Zr (IV) and Hf (IV) solution was developed at pH 6 and later at pH 4, zirconium ions was determined only. The difference of the absorbance would represent the amount of Hf.

In this respect, the organic compound (BrPhPQ) and its complexes with Zr (IV) and Hf (IV) were investigated using IR technique to compare their differences in the peak positions and intensities at acidities. The data are documented in TABLE 1 and featured in Figures 11-14, it describes the spectral data of the following:

- (1) The organic compound (BrPhPQ) in ethanol/N,N dimethyl formamide.
- (2) The formed Zr-BrPhPQ complex at pH 6.
- (3) The formed Hf-BrPhPQ complex at pH 4 and 6.

Results outlined in TABLE 2 demonstrated that both Zr (IV) and Hf (IV) formed complexes with the synthesized reagent at pH 6 whereas the amino group NH_2 consumed. On the contrary, Hf-BrPhPQ complex was not formed at pH 4, i.e the amino group appeared.

An experiment was carried out to determine Hf (IV) in presence of Zr (IV) through control of acidity of synthetic mixtures of the two metal ions in different proportional. The results obtained in TABLE 3 indicate high accordance between individual metal cations and synthetic mixtures of Zr (IV) and Hf (IV) species at pH 4 and 6. It can readily be assumed that the determination of Hf (IV) in presence of Zr (IV) or vice versa would be possible.

TABLE 2 : IR spectral data of Zr and Hf complexes.

Major groups	(BrPhPQ) (vs)	Zr-(BrPhPQ) (m)	Hf-(BrPhPQ) (m)	
		pH 6	pH 6	pH 4
Aliphatic				
C – H	2977.9	2978.9	2978.9	2978.9
C = O	1716.5	1651.0	1636.3	1716.5
C = N	1639.4	2102.3	2077.9	1639.4
N = N	1928.7	1959.5	1928.7	1959.5
N – H	3363.9	3274.9	3434.6	3363.9
NH ₂	3664.5	---	---	3664.5
C – Br	671.2	667.3	658.57	971.2

vs: very strong; m: moderate

TABLE 3 : Absorbance analysis of the individual and mixed complexes.

Constituent	Absorbance		S.D
	pH 6	pH 4	
0.250 $\mu\text{g/ml}$ Zr ⁴⁺	0.463	0.462	0.005
0.050 $\mu\text{g/ml}$ Hf ⁴⁺	0.075	-	0.040
0.025 $\mu\text{g/ml}$ Hf ⁴⁺	0.036	-	0.050
0.25 $\mu\text{g/ml}$ Zr ⁴⁺ + 0.05 $\mu\text{g/ml}$ Hf ⁴⁺	0.540	0.462	0.07
0.25 $\mu\text{g/ml}$ Zr ⁴⁺ + 0.025 $\mu\text{g/ml}$ Hf ⁴⁺	0.498	0.462	0.09
0.25 $\mu\text{g/ml}$ Zr ⁴⁺ + 0.0125 $\mu\text{g/ml}$ Hf ⁴⁺	0.480	0.462	0.08
0.375 $\mu\text{g/ml}$ Zr ⁴⁺ + 0.0125 $\mu\text{g/ml}$ Hf ⁴⁺	0.711	0.694	0.1
0.75 $\mu\text{g/ml}$ Zr ⁴⁺ + 0.0125 $\mu\text{g/ml}$ Hf ⁴⁺	1.404	1.386	0.11

Effect of foreign ions

The effect of foreign ions on the determination of 0.250 $\mu\text{g/ml}$ Zr⁴⁺ and 0.05 $\mu\text{g/ml}$ Hf⁴⁺ were studied by the use of the proposed method at optimum conditions. The criterion for interference^[26] was an absorbance value varying by more than $\pm 5\%$ from the expected value for Zr (IV) and Hf (IV). The results are summarized, in TABLE 4. The results show that, all ions have no significant effect on the determination of Zr (IV) and Hf (IV). The quantities of these diverse ions mentioned were the actual amounts added and not the tolerance limits. Common ions (U^{6+} , Th^{4+} , Nb^{5+} and Ti^{4+}) suspected to be in the analyte zircon solution were tested using standard solution of Zr (IV) and Hf (IV). The obtained results indicated that the latter studied metal ions do not impart any interfering effect up to 5 $\mu\text{g/ml}$. Also, silicate, phosphate and chloride anions had no effect on Zr (IV) and Hf (IV) measurement.

Application

The optimized method using BrPhPQ reagent was

applied for direct determination of Zr and Hf elements in zircon. It is the common primary ore for the production high purity grade Zr metal and its main occurrence in Egypt is as constituent of beach black sands along with ilmenite and monazite. It is separated from other heavy minerals by using wet gravity concentration followed by magnetic separation. The chemical analysis of the given sample in comparison with other published values is presented in TABLE 5.

The results obtained for spectrophotometric and ICP/OES techniques indicate high concordance with their published values.

TABLE 4 : Table of tolerance limits* of foreign ions, tolerance ratio. [Species (x)]/ metal ion (w/w).

Species X	Tolerance ratio X/Zr ⁴⁺	Tolerance ratio X/Hf ⁴⁺
U ⁶⁺	20	100
Th ⁴⁺	20	100
Nb ⁵⁺	20	100
Ti ⁴⁺	20	100
Al ³⁺	20000	100000
Fe ³⁺	20000	100000
P ⁵⁺	4000	20000
Cl ²⁻	400	2000
SO ₄ ²⁻	400	2000

*Tolerance limit was defined as ratio that causes less than 5 percent interference.

TABLE 5 : Chemical analysis of Egyptian zircon sand.

Compound	Percent (by weight)		Ref 27**
	Present work Spectrophotometer	ICP/OES*	
ZrO ₂	65.29	65.30	66.42
HfO ₂	1.15	1.10	
SiO ₂	31.5		32.23
Fe ₂ O ₃	0.10		0.14
P ₂ O ₅	0.15		
TiO ₂	0.07		
ThO ₂	0.02		0.02
U ₃ O ₈	0.02		0.04

* Central Laboratory for Elemental and Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority; ** using spectrophotometer

CONCLUSION

The present work results suggest a new reagent for the selective determination of Hf (IV) in presence of Zr

(IV). Systematic studies were performed to develop the synthesized reagent for the quantitative determination of the two elements in aqueous solution. The high stability of the formed complexes of the two elements permits the elements determination at high dilution. Spectrophotometry, the procedure described was believed simple, rapid and sensitive enough to determine Zr and Hf in zircon mineral. The accuracy and precision have shown to be adequate for zircon matrices.

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