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Research Note

Extractive spectrophotometric determination of Zirconium with 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one as an analytical reagent

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Abstract-An extractive spectrophotometric method is developed for the trace determination of zirconium. A yellow colored complex is formed by 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one (CHPC) with zirconium (IV) which is quantitatively extracted into dichloromethane. The method obeys Beer's law in the range 0.0-5.0 $\mu\text{g Zr mL}^{-1}$, having molar absorptivity, specific absorptivity and Sandell's sensitivity of $5.930 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.650 \text{ mL g}^{-1} \text{ cm}^{-1}$ and $0.00153 \mu\text{g of Zr cm}^{-2}$ respectively at 415 nm. The method is free from the interferences of Be(II), La(III), Dy(III), Cr(VI), Ba(II), Se(IV), Re(VII), Mn(II), Bi(III) Co(III), Ce(IV), Hg(II), Ca(II), Sr(II), Cd(II) and many other analytically important elements. The method has good reproducibility and can be satisfactorily applied to determination of zirconium in various samples of different complexity.

Keywords-Zirconium (IV), 6-Chloro-3-hydroxy-2-phenyl-4H-chromen-4-one (CHPC), spectrophotometry, absorption

INTRODUCTION

Though various organic reagents¹⁻⁷ have often been employed for the spectrophotometric determination of zirconium, but their applicability is seriously impaired mainly due to gross interferences and for want of sensitivity too. There is still a great demand for more specific methods of analysis with improved sensitivity and selectivity for the analysis of metal ion in various technical samples. Keeping in mind the idea of sensitivity and selectivity, a benzopyran derivative 6-chloro-3-

hydroxy-2-phenyl-4*H*-chromen-4-one (CHPC) is used for improving the desirable characteristics of the spectrophotometric methods for the determination of zirconium (IV) employing extractive techniques.

EXPERIMENTAL

Reagents and solutions: A stock solution of zirconium (IV) containing 1mg mL⁻¹ was obtained by dissolving an accurately weighed amount of ZrOCl₂.8H₂O in minimum volume of conc. HCl and made up the volume up to 100 mL in a volumetric flask before standardizing the metal ion gravimetrically⁸. Lower concentrations at µg mL⁻¹ level were prepared by proportionate dilutions of this solution.

Similarly, stock solutions of other metal ions at the mg mL⁻¹ level were prepared by dissolving their commonly available sodium or potassium salts ‘chemically pure’ grade in deionized water or dilute acid. Dichloromethane used is of AR grade.

The reagent 6-chloro-3-hydroxy-2-phenyl-4*H*-chromen-4-one⁹ (CHPC) (Fig.1)0.05% (m/v), was prepared by dissolving it in alcohol.

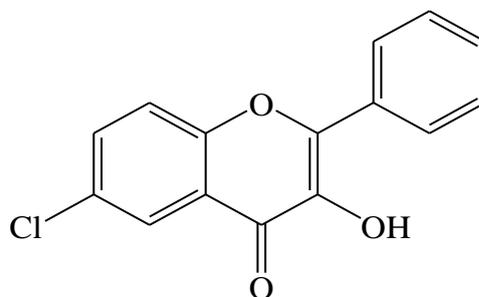


Fig.1:6-Chloro-3-hydroxy-2-phenyl-4*H*-chromen-4-one (CHPC)

Synthetic sample solutions are obtained by mixing solutions of Zr(IV) and other metal ions in a suitable proportion with compositions as shown in Table.1

Table.1: Analysis of different samples by the proposed method

Sample composition	Zr(IV) added(µg)	Zr(IV) found(µg) [#]
Cd ^{II} (5), La ^{III} (1), Mg ^{II} (2),	10.0	09.98
Sr ^{II} (1), Se ^{IV} (1), Zn ^{II} (1),	15.0	15.45
Co ^{III} (1), Ca ^{II} (1), Ba ^{II} (1),	10.0	09.52
Re ^{VII} (0.1), Rh ^{III} (0.1), Bi ^{III} (0.1),	20.0	19.89
Hg ^{II} (1), Cd ^{II} (2), Ca ^{II} (1),	20.0	20.62
La ^{III} (0.1), Mg ^{II} (1), Nd ^{III} (1),	30.0	29.95
Be ^{II} (0.1), Se ^{IV} (0.1), Hg ^I (0.1),	15.0	15.12
Hg ^I (0.1), Rh ^{III} (0.1), Ca ^{II} (0.1),	10.0	10.02
Reverberatory flue dust, 50mg	30.0	29.54
Tap water	20.0	19.75

* Figure in parenthesis indicates the amount of the metal in mg

Average of triplicate analysis.

Reverberatory flue dust: Sample from copper manufacture is mixed with known amount of zirconium content and dried in oven. After fusion of sample with sodium peroxide (approximately 8 times the weight of sample), the leach is neutralized carefully with conc.H₂SO₄ and finally made alkaline. Then filtered off hydroxide precipitates, followed by 4-5 washing with distilled water. The filtrate along with the washings is adjusted at pH~7 made up to mark with water and zirconium determined as described below in the procedure. For the absorbance measurement and spectral studies, a UV-visible spectrophotometer (Systronic -166) is used.

Procedures: To an aliquot containing 10 µg in a 100 ml separating funnel, add 0.8 ml HCl(1M), 1.5 ml 0.1% CHPC(in ethanol) and enough deionized water to make the final aqueous volume 10 ml.It is equilibrated once with an equal volume of dichloromethane for 30 sec, releasing the pressure occasionally through the stop cork. After phase separation, the organic layer is filtered through Whatman filter paper number 41 (pretreated with DCM) in a 10 ml volumetric flask which is made up to mark with pure dichloromethane and the absorbance of the yellow complex is measured at 415 nm against the reagent blank prepared in an analogous manner. The amount of zirconium is determined from the calibration curve obtained by plotting a graph between micro amounts of Zr(IV) and the corresponding absorbance values obtained under optimum conditions of procedure.

Result and discussion: Zr(IV) reacts with CHPC in acidic medium forming a yellow colored species which is quantitatively extracted into dichloromethane. Absorption maximum of the complex lies at 413-417 nm in visible region, where the reagent blank shows minimal absorbance (**Fig.2**).Hence, the absorbance measurements of the system are carried out at 415 nm.

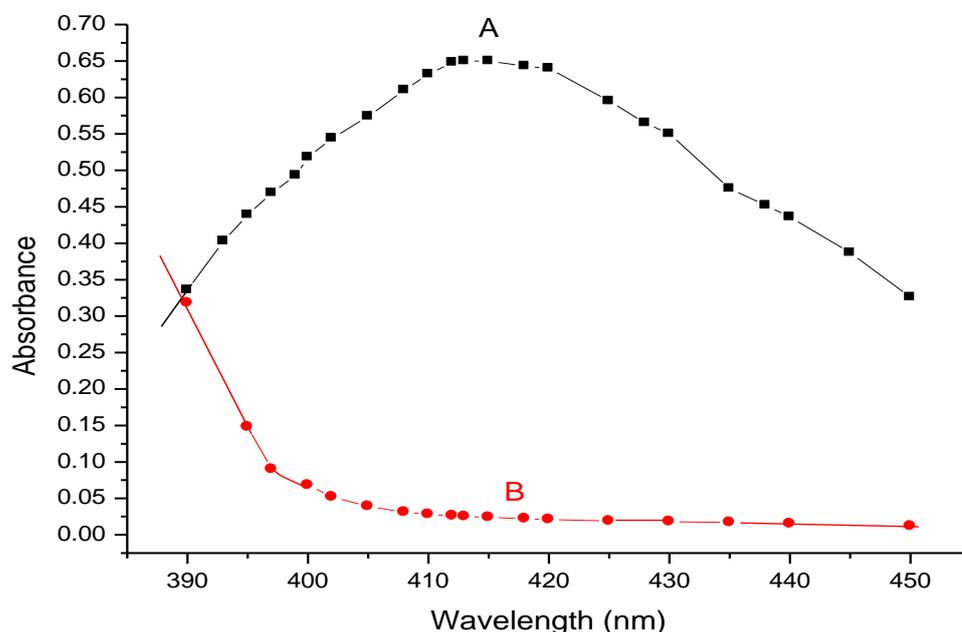


Fig.2: Absorbance spectrum of Zr(IV)-CHPC in dichloromethane.
(A) 1 µg/mL⁻¹ zirconium measured against reagent blank.
(B) Reagent blank measured against dichloromethane.

The effect of various parameter influencing the formation of metal complex (molarity of HCl, concentration of CHPC and equilibration time) are given in Table -2

Table-2: Effect of various parameters on the absorbance on Zr (IV)-CHPC complex

HCl (M) ^a , mL	0.2	0.4	0.6	0.8-1.0	1.2	1.5	1.8
Absorbance	0.399	0.457	0.590	0.650	0.648	0.630	0.617
CHPC ^b , mL	0.2	0.5	1.0	1.2	1.4-1.6	1.8	2.0
Absorbance	0.195	0.357	0.553	0.625	0.650	0.645	0.633
Equilibration time ^c , sec.	2	5	10	15-60			
Absorbance	0.282	0.496	0.590	0.650			

Conditions:

- Zr (IV) = 10 µg, CHPC (0.05% in ethanol) = 2 mL, HCl (1M) = variable, aqueous volume = solvent volume = 10 mL, solvent = DCM, equilibration time = 30 sec., no. of extraction = 1, λ_{\max} = 415 nm.
- HCl (1M) = 0.8 mL, other condition being the same as in (a) expect for the variation in reagent concentration.
- CHPC (0.05 % in alcohol) = 1.5 mL, other condition being the same as in (b) expect for the variation in equilibration time.

The absorbance of complex is affected with different organic solvents (formed under conditions of procedure. The absorbance of Zr(IV)-CHPC complex in different solvents are in order:

Dichloromethane > Chloroform > Dichloro ethane > Carbon tetrachloride > *iso*Butyl methyl ketone > Toluene > Amyl alcohol > Benzene > Xylene > Cyclohexane.

The absorbance of the complex is higher in dichloromethane. Hence, all the measurements are carried out in dichloromethane.

Spectral characteristics, Beer's law and Sandell's sensitivity: The complex of Zr (IV)-CHPC complex extracted for 30 sec in dichloromethane at 415 nm, where the absorbance of blank is quite low (Fig-2). Therefore, all the absorbance measurements have been carried out at 415 nm. Beer's law is obeyed in the range of 0.0-5.0 µgZr mL⁻¹. Molar absorbtivity, specific absorbtivity and Sandell sensitivity of the method are 5.930 × 10⁴ L mol⁻¹ cm⁻¹, 0.650 mL g⁻¹ cm⁻¹ and 0.00153 µg Zrcm⁻², respectively at 415 nm respectively.

Effect of diverse ions: The effect of different anions and complexing agent has been studied on the absorbance of the complex under the optimum condition of the procedure. The anions and complexing agent added as their sodium or potassium salts in aqueous phase (mg/10mL) such as Bromide,

thiocyanate (100mg each); nitrate, thiourea, iodide (50mg each); ascorbic acid, sulphate(25 mg); acetate (10mg) and citrate, tartrate (1mgeach) do not interfere. However oxalate, EDTA and phosphate interfere seriously. Also under optimum condition of procedure, in 10 mL aqueous volume, Ca(II), La(III), Pr(III), Ho(III), Cd(II), Mg(II),Dy(III), Hg(II), Hg(I) (10 mg each); Se(IV), Eu(III), Nd(III), Zn(II), Sr(II), Mn(II) (5mg each); Co(III), Rh(III), Re(VII), (2mg each); Sb(III), Ni(II), Ba(II), Pt(IV) (1mg each) and Pb(II), Bi(III), TI(I) (0.1 mg each) do not interfere in the absorbance of complex.

Stoichiometry of the extracted species: The ratio of the Zr (IV) and CHPC in the complex is determined by Job's method of continues variation¹⁰as modified by Vosburgh and cooper¹¹by taking their equimolar solution ($5.5 \times 10^{-4}M$) according the procedure mentioned above. The ratio of Zr(IV)and CHPC is further confirmed by mole ratio method¹² using equimolar solution of Zr(IV) and CHPC($5.5 \times 10^{-4}M$). The absorbance's are measured at 410, 415 and 420 nm and metal to ligand ratio is 1:2 in the extractive species.

Application: The wide applicability of the method is tested by carrying out satisfactorily the analysis of several synthetic and natural samples. The proposed method is simple, rapid, sensitive and free from the interferences of a large number of metal ions of great analytical importance. The validity of the method is tested by satisfactorily analysis of a variety of samples.

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