Trace determination of zirconium with 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one by solvent extraction

Monica Nijhawan, Anoop Kumar Chhakkar & Lajpat Rai Kakkar*
Department of Chemistry, Kurukshetra University, Kurukshetra 136119 (Haryana), India
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3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one forms a yellow coloured complex with zirconium at pH 8-8.2 which is quantitatively extracted into 1,2-dichloroethane with absorption maximum at 425nm. The method obeys Beer’s law in the range 0-10 μg Zr(IV)/10ml and has a Sandell’s sensitivity of 0.0012 μg Zr cm⁻².

Although a number of separations with specific modifications, wherever necessary, have resulted from the application of solvent extraction using hydroxy chromone derivatives for the complexation of zirconium and other metal ions, still it has been considered necessary to study the behaviour of zirconium with respect to one of its derivatives, 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one with a view to develop a highly sensitive spectrophotometric method for the determination of trace amounts of zirconium.

Experimental
A standard stock solution of zirconium is prepared by dissolving an accurately weighed amount of ZrOCl₂.8H₂O in 2.0 M HCl to give 1mg Zr/ml. Lower concentrations of the metal ion at μg/ml level are obtained by suitable dilutions. Solutions of other metal ions (<10mg/ml) are prepared by dissolving their commonly available chemically pure salts in water or dilute acids (HCl or H₂SO₄) or sodium bicarbonate, 1N.

3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one (HTC) is synthesised. 0.05% (W/V) solution of the reagent is prepared in distilled ethanol. 1,2-Dichloroethane (Qualigen) was distilled and the fraction distilling between 83-84°C was collected for use.

Samples: Synthetic samples are prepared by mixing zirconium and other metal ion solutions as shown in Table I.

Procedure
To an aliquot containing 10μg Zr in a 100ml separatory funnel, add 1.8ml of 0.05% 3-hydroxy-2-(2'-thienyl)-4H-chromen-4-one (HTC) regent and 0.2ml 1N NaHCO₃ in a final 10ml aqueous volume (pH 8.0-8.2). It is equilibrated once with an equal volume of 1,2-dichloroethane for 60s, releasing the pressure occasionally through the stopcock. After phase separation, the organic layer is filtered through Whatman’s paper No. 41 (pretreated with 1,2-dichloroethane) to remove water droplets, if any, into a 10ml volumetric flask which is then made up to the mark with the pure solvent and the absorbance is measured at 425nm against reagent blank using 10mm matched cells on a UV-visible (Shimadzu-140-02) spectrophotometer.

For samples also containing 100 μg each of Cr(VI), Mo(VI), W(VI), addition of 50mg sodium fluoride is necessitated in order to mask them separately just before effecting extraction with the solvent.

Finally, zirconium content is determined from the calibration curve prepared under optimum conditions of the procedure.

Results and discussion
It has been observed that zirconium in the tetravalent state, reacts with HTC forming a yellow complex in neutral medium. The intensity of the coloured species increases on making the solution slightly alkaline with NaHCO₃ (pH 8.0-8.2).

The effect of various parameters influencing the formation of metal complex, namely, NaHCO₃, HTC, equilibration time, is shown in Table 2 and the optimum

### Table 1 — Analysis of samples by the proposed method

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Matrix</th>
<th>Sample composition</th>
<th>Zr added (μg)</th>
<th>Zr Found (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>V(1000)</td>
<td></td>
<td>10</td>
<td>11.00</td>
</tr>
<tr>
<td>2.</td>
<td>Zr(200), Ru(10), U(500)</td>
<td></td>
<td>9</td>
<td>9.9</td>
</tr>
<tr>
<td>3.</td>
<td>U(1000)</td>
<td></td>
<td>7</td>
<td>6.4</td>
</tr>
<tr>
<td>4.</td>
<td>Zn(1000), Cd(100), U(1000)</td>
<td></td>
<td>6</td>
<td>6.4</td>
</tr>
<tr>
<td>5.</td>
<td>Ni(500), Ru(20)</td>
<td></td>
<td>5</td>
<td>5.2</td>
</tr>
<tr>
<td>6.</td>
<td>Cr(VI)(50), Mo(20), W(20)</td>
<td></td>
<td>5</td>
<td>5.5</td>
</tr>
<tr>
<td>7.</td>
<td>Ag (200)</td>
<td></td>
<td>2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Figure in brackets indicates the amount of metal ions in μg. (a) In presence of fluoride; (b) In presence of chloride; (c) Average of triplicate results.
Table 2—Effect of various parameters on the absorbance of zirconium (IV)-HTC complex

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
<th>Absorbance</th>
<th>Absorbance</th>
<th>Absorbance</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO$_3$ (1N), ml</td>
<td>0.1-0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>3-Hydroxy-2-(2'-thieryl)-4H-chromen-4-one, ml</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Equilibration Time, sec</td>
<td>5</td>
<td>10</td>
<td>15-180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaHCO$_3$ (1N)</td>
<td>0.2 ml</td>
<td>0.3 ml</td>
<td>0.5 ml</td>
<td>0.7 ml</td>
<td>1.0 ml</td>
</tr>
<tr>
<td>HTC (0.05% in ethanol)</td>
<td>1.5 ml</td>
<td>2.0 ml</td>
<td>2.5 ml</td>
<td>3.0 ml</td>
<td>4.0 ml</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.017</td>
<td>0.19</td>
<td>0.30</td>
<td>0.53</td>
<td>0.74</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.19</td>
<td>0.30</td>
<td>0.53</td>
<td>0.74</td>
<td>0.79</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.785</td>
<td>0.805</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conditions:
(a) Zr(IV) = 10µg, HTC (0.05% in ethanol) = 1.5 ml, NaHCO$_3$ (1N)= variable, aqueous volume = solvent volume = 10 ml, solvent = dichloroethane, equilibration time = 1 min, number of extractions = 1, absorbance measured at 425 nm against reagent blank.
(b) NaHCO$_3$ (1N) = 0.2 ml, other conditions are same as in (a) except the variation of HTC.
(c) 3-Hydroxy-2-(2'-thieryl)-4H-chromen-4-one (0.05% in ethanol) = 1.8 ml, other conditions are same as in (b) except the variation in equilibration time.

On adjusting the pH of the solution with NaOH, the extraction was found to be incomplete; whereas, low absorbance values were obtained with Na$_2$CO$_3$. However, the extraction of the complex was quantitative with relatively high absorbance value in case of NaHCO$_3$ thus the choice.

The extraction of the complex (formed under conditions of the procedure) with 1,2-dichloroethane was quantitative in one contact and no trace of zirconium was left in the aqueous phase as confirmed on testing by arsenazo III method. The complex is quite stable in 1,2-dichloroethane with maximum absorbance value. The absorbance of the complex is found to decrease in case of other solvents in the order as indicated-benzene, carbon tetrachloride, chloroform, isobutylmethyl ketone, amylacetate, amyl alcohol, butyl acetate. Thus, use of 1,2-dichloroethane as extracting solvent for the complex in this system is preferred.

Spectral characteristics, Beer's law and Sandell's sensitivity

The absorption spectrum of Zr(IV)-HTC complex in 1,2-dichloroethane and that of the reagent blank under identical conditions is shown in Fig. 1, indicating $\lambda_{max}$ for the complex at 425 nm. Hence, all absorbance measurements throughout the system are made at 425 nm. Beer's law is obeyed in the range 0.0-1.0 µg Zr/ml and the optimum concentration range that can be measured accurately, as evaluated from Ringbom's plot (Fig. 2), is 0.20 to 0.95 ppm Zr(IV). The molar absorptivity and Sandell's sensitivity are indicated in Fig. 1.

Fig. 1—Absorption spectrum of the Zr(IV)-HTC complex in dichloroethane. [Curve A: 1µg Zr(IV) ml$^{-1}$ measured against reagent blank. Curve B: Reagent blank measured against pure dichloroethane. NaHCO$_3$ (1N)=0.2 ml, HTC (0.05%)=1.8 ml, aqueous volume=sovent volume=10 ml, solvent=dichloroethane, equilibration time=60 s]

Fig. 2—Ringbom plot for Zr(IV)-HTC complex. [NaHCO$_3$ (1N)=0.2 ml, HTC (0.05%)=1.8 ml, aqueous volume=solvent volume=10 ml, solvent=1,2-dichloroethane, equilibration time=60 s]
sensitivity of the system are $7.52 \times 10^4 \text{mol}^{-1} \text{cm}^{-1}$ and $0.0012 \mu \text{g Zr cm}^{-2}$, respectively. For ten replicate determinations containing $10 \mu \text{g Zr}$ each time, the standard deviation is found to be $+0.004$ and relative standard deviation is $0.48\%$.

**Effects of diverse ions**

The extraction of Zr(IV)-HTC complex has been studied in the presence of various anions and complexing agents. $\text{NO}_3^-$, $\text{Cl}^-$, $\text{F}^-$ (50mg each); $\text{C}_2\text{O}_4^{2-}$, (10mg); $\text{CH}_3\text{COO}^-$, $\text{SO}_4^{2-}$, (2mg each); added prior to the addition of the reagent to the aqueous phase (10ml), do not affect the absorbance of Zr(IV) complex; whereas, $\text{PO}_4^{3-}$, $\text{I}^-$, $\text{SO}_4^{2-}$, EDTA, citrate and ascobic acid interfere even when present in small amounts.

Also under optimum conditions of the procedure, in 10ml aqueous volume, $\text{Ca (II)}$, $\text{Sr(II)}$, $\text{Mg(II)}$, $\text{Mn(II)}$, each 10mg; $\text{Ba(II)}$, $\text{Cr(III)}$, each 5mg; $\text{U(VI)}$, 4mg; $\text{Zn(II)}$, $\text{Ni(II)}$, $\text{Co(II)}$, $\text{Hg(II)}$, $\text{V(V)}$, each 1mg; $\text{Cd(II)}$, 0.5mg; $\text{Ru(III)}$, $\text{Au(III)}$, $\text{Ta(V)}$, each 0.1mg; $\text{Pt(IV)}$, $\text{Ir(III)}$, each 0.02mg; do not show any absorbance. The interference due to $\text{Cr(VI)}$, $\text{Mo(VI)}$ and $\text{W(VI)}$, 0.1 mg each, are removed by adding fluoride (50mg NaF) and that of $\text{Ag(I)}$, 0.1mg, by adding chloride (50mg NaCl).

**Stoichiometry of the extracted species**

The ratio of Zr(IV) to HTC in the extracted species is determined by Job's method of continuous variations as modified by Vosburgh and Cooper using equimolar solutions of Zr and HTC ($1.096 \times 10^{-4} \text{M}$). The absorbances are measured at 410, 425 and 440nm. The three curves obtained by plotting mole fraction of Zr against the respective absorbance values indicate a maximum corresponding to metal to ligand ratio of 1:3 in the extracted species. The mole ratio method also confirms this conclusion. The probable structure of the complex is as shown below:

**Applications**

The applicability of the proposed method is tested by carrying out satisfactorily analysis of various samples with reproducible results (Table 2). The method is free from interference of a large number of metal ions of great analytical importance so far as the determination of zirconium is concerned, and has an edge over some of the existing methods (Table 3) in respect of its sensitivity, selectivity and accuracy.

**Acknowledgement**

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**References**