

## Ti(IV) Complexes with Cinnamohydroxamic Acid & Its Extractive Spectrophotometric Determination in Trace Amounts

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Cinnamohydroxamic acid forms with Ti(IV) different complexes at different acid concentrations. A 1:3 (metal: ligand) complex is formed in the pH range 0.8-1.4 whereas 1:2 and 1:1 complexes are produced at 2.4-5N and 7.5-9N HCl respectively. A procedure for determination of trace amounts of titanium by spectrophotometric methods followed by solvent extraction is described. The stepwise as well as overall formation constants of the complexes have been calculated.

THE use of benzophenyl hydroxylamine (BPHA) and its several N-substituted analogues as analytical reagents has been extensively reviewed<sup>1-5</sup>. But very little attention has been paid to the parent hydroxamic acids and to their ability to form different complexes at different acidities<sup>6-9</sup>. The present paper deals with simultaneous solvent extraction and spectrophotometric investigation of Ti(IV) complexes at different acid concentrations with cinnamohydroxamic acid (CHA). CHA forms 1:3, 1:2 and 1:1 metal-ligand complexes with Ti(IV) in the pH range of 0.8-1.4 and acidity range of 2.4-5N and 7.5-9N HCl respectively. The metal to ligand ratios have been established by Job's and molar ratio methods. The formation constants of the complexes have been evaluated by Yatsimirskii's<sup>10</sup>, Leden's<sup>11</sup> and Harvey-Manning's<sup>12</sup> procedures and compared. The molar absorptivity, sensitivity and range have been calculated and suitability of the reagent for analytical determination of microamounts of titanium in the presence of diverse ions have been described. The molar absorptivity data have been compared with some most sensitive reagents reported in literature.

### Materials and Methods

**Reagents and solutions**—A stock solution of titanium (2.18 mg/ml) was prepared from potassium titanyl oxalate (AR) and was standardized<sup>13</sup>. Metal solutions of desired dilution were obtained from the stock solution. The reagent, CHA (m.p. 110-111°), was prepared following the method described in literature<sup>14</sup>. Standard reagent solutions of desired strength in AR isoamyl alcohol were used. Other chemicals and solvents used were of AR or specpure quality.

**Apparatus**—Spectrophotometric measurements were carried out on a Hilger Uvispek spectrophotometer with matched 1 cm glass cells. A Cambridge pH meter (bench-type) was used for pH measurements. IBM 1130 scientific and electronic computer, using FORTRAN programming, was employed for evaluation of the formation constants (1:3 system).

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**Extraction procedure**—An aliquot of titanium solution ( $8.352 \times 10^{-5}M$ ) was adjusted to desired acidity viz. 4N or 8N HCl or pH 1.1. To 15 ml of the aqueous phase was added a desired amount of the reagent solution (0.12M) in isoamyl alcohol. The volume of the nonaqueous phase was maintained equal to that of the aqueous phase. After shaking thoroughly for 5 min to reach equilibrium, the yellow coloured nonaqueous layer was withdrawn. The aqueous phase was shaken with a further 5 ml of isoamyl alcohol. The combined extract after drying ( $Na_2SO_4$ ) was diluted to 25 ml with isoamyl alcohol. The absorbance of the solution was measured at 410 nm against reagent blank.

### Results and Discussion

**Absorption spectrum**—The spectra of the complex solutions at 4N and 8N HCl, showed maximum absorption at 390 and 360 nm respectively, while that of complex solution at pH 1.1 showed gradual decrease in value in the said range. As the reagent absorption was found to be appreciably low around 410 nm, all absorbance measurements were made at 410 nm against the reagent blank.

**Effect of reagent concentration**—A single extraction of a fixed amount of titanium with 10 ml, 8 ml and 4 ml of 0.12M CHA at pH 1.1, 4N and 8N HCl respectively were quite adequate for a quantitative extraction. The colour of the complexes was found to be stable for about 24 hours.

**Effect of acid on composition of the complexes**—Yellow titanium complexes of CHA are extractable into isoamyl alcohol from pH 0.5 to 9N HCl. Absorbances of different sets of complementary solutions (Job's method), measured at 410 nm, revealed that the complexes are predominantly 1:3 at pH 1.1, 1:2 at 4N and 1:1 at 8N HCl. The strengths of equimolar metal and reagent solutions were  $2.116 \times 10^{-2}M$  at the first two acidities and  $1.904 \times 10^{-2}M$  at 8N HCl. Similar results were confirmed by molar ratio methods using equimolar solutions of  $1.587 \times 10^{-2}M$ ,  $2.116 \times 10^{-2}M$  and  $1.904 \times 10^{-2}M$  at the respective acidities.

**Calibration curve, optimum range and photometric error**—The concentration ranges in conformity to Beer's law were found to be 1-9 ppm at pH 1.1,

1.8 ppm at 4N HCl and 0.5-10 ppm at 8N HCl. The optimum concentration ranges from Ringbom's curves were 3.9 ppm, 3.8 ppm and 3.10 ppm respectively with relative analysis error per one per cent absolute photometric error of 2.74 at all the acidities.

**Molar absorptivity and sensitivity** — The molar absorptivity of the complexes, calculated from Beer's law data at 410 nm, are  $(2.63 \pm 0.01) \times 10^3$ ,  $(3.33 \pm 0.11) \times 10^3$  and  $(3.35 \pm 0.04) \times 10^3$  at pH 1.1, 4N and 8N HCl respectively, while those at the respective  $\lambda_{max}$  are  $5.03 \times 10^3$  (390 nm) at 4N HCl and  $8.02 \times 10^3$  (360 nm) at 8N HCl. The Sandell's sensitivity values are 0.02  $\mu\text{g}$  per  $\text{cm}^2$ , 0.015 and 0.013  $\mu\text{g}$  per  $\text{cm}^2$  respectively. The molar absorptivity values have been compared with those of reported highly sensitive reagents<sup>5,15-21</sup> (Table 1).

**Effect of foreign ions** — The ions, commonly associated with titanium, in moderate concentrations were found to be tolerable. The ions Fe(III), U(IV) and V(V) were found to interfere at 410 nm.

**Formation constants of the complexes** — Stepwise formation constants for all the systems were calculated following the method of Yatsimirskii<sup>10</sup> and Leden<sup>11</sup>. The equilibrium ligand concentrations and the degree of complex formation were calculated

from data of molar ratio plots with the help of Beer's law data. Construction of suitable functions\* and their evaluation were made in the manner stated earlier<sup>12</sup>. The values of  $K_1$ ,  $K_2$  and  $K_3$  of 1:3 system, related with the said functions by the following equations (Eqs. 1-3), were evaluated, solving a fourth degree polynomial equation<sup>22</sup> in  $K_2$  by FORTRAN programming on a scientific and electronic computer (IBM 1130), initial guess value of  $K_2$  being provided by Newton-Raphson's method. The stepwise stability constants and the values of the overall stability constants by Harvey-Manning's method are given in Table 2.

$$a_1 = \epsilon_1 K_1; \quad b_1 = \epsilon_3 \quad \dots(1)$$

$$a_2 = \epsilon_2 K_1 K_1 - \epsilon_1 K_1^2; \quad b_2 = \frac{\epsilon_2 - \epsilon_3}{K_2} \quad \dots(2)$$

$$a_3 = \epsilon_1 K_1 K_1 K_3 - \epsilon_1 K_1^3; \quad b_3 = \frac{\epsilon_1 - \epsilon_2}{K_2} \quad \dots(3)$$

In the pH as well as the normality range of acidity, titanium exists in the form of  $\text{TiO}^{2+}$  as evidenced from the formula of the isolated complexes<sup>23-25</sup>. On the basis of data in Table 2, the formula of 1:2 complex may be proposed as  $[\text{TiOR}_2]$  where HR stands for CHA. From formation constant data, the probable formula of 1:3 complex is  $[\text{TiOR}_2]\text{HR}$ , where HR may be in resonance with the other two in such a way that always two ligand molecules are attached to titanium atom as bidentate unit and the third one is associated through titanyl oxygen atom. Increase in acidity brings about gradual replacement<sup>26</sup> of ligand molecule till the formation of 1:1  $[\text{TiORCl}]$  at 8N HCl.

It is apparent from the present study that lower metal to ligand complexes are favoured with increase in acidity. And microamounts of titanium can be determined at 4N and 8N HCl by CHA.

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TABLE 1 — MOLAR ABSORPTIVITY OF Ti(IV) COMPLEXES WITH DIFFERENT LIGANDS

Ligand	Acidity	Absorption maximum nm	Molar absorptivity
Salicylfluorone <sup>15</sup>	pH 1.0	520	$9.2 \times 10^4$
Trihydroxy-9-methyl-6-fluorone <sup>16</sup>	pH 1.7-2.1	520	$6.04 \times 10^4$
1-(2-Pyridylazo)-2-naphthol <sup>12</sup>			$1.74 \times 10^4$
Xylethol orange <sup>15</sup>	pH 2.9	560	$1.2 \times 10^4$
3-Hydroxy-1-(p-sulphonato phenyl)-3-phenyl-triazine <sup>15</sup>	pH 1.9-3.3	405	$1.65 \times 10^4$
Tribromopyrogallol* + diantipyryl-methane <sup>19</sup>	0.5N HCl	400	$(1.55 \pm 0.03) \times 10^4$
Indoferron* + 1,3-diphenyl guanidium cation <sup>20</sup>	pH 2.5-3.5	600	$1.8 \times 10^4$
N-Benzoylphenyl hydroxylamine* + $\text{NH}_4\text{SCN}$ <sup>5,21</sup>	10N HCl	352	$1.54 \times 10^4$
Cinnamohydroxamic acid (CHA)	4N HCl	390	$5.03 \times 10^3$
	8N HCl	360	$8.02 \times 10^3$

\*Ternary systems.

TABLE 2 — STEPWISE STABILITY CONSTANTS FOR TITANIUM COMPLEXES AT  $27^\circ \pm 2^\circ$

Method	1:3 complex				1:2 complex			1:1 complex
	log $K_1$	log $K_2$	log $K_3$	log $\beta_3$	log $K_1$	log $K_2$	log $\beta_2$	log $K$
Yatsimirskii's	2.13*	2.74*	2.44*	7.31	2.23	2.36	4.59	2.50
Leden's	—	—	—	—	1.82	2.33	4.15	2.48
Harvey and Manning's	—	—	—	7.92	—	—	4.72	2.39

\*Values from computer.

\*Values of subsidiary functions for 1:3 system (Yatsimirskii's method) and of 1:2 system (Leden's method) can be had from the authors on request.

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