

$\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ , citric acid and gum acacia (20 mg each) have no influence on the stoichiometry of oxidation of isoniazid. But any species oxidised by excess of CAT or CAB will interfere.

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### Extraction & Spectrophotometric Determination of Nb(V), Ta(V) & Ti(IV) with 2'-Hydroxy-4-methoxy-5'-methylchalkone Oxime

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A method is described for the extraction and spectrophotometric determination of Nb(V), Ta(V) and Ti(IV) using 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) in chloroform. The yellow coloured complexes formed are quantitatively extractable from hydrochloric acid medium in the presence of thiocyanate. The Beer's law is obeyed in a wide range of concentrations. The metal ions under study can be separated and determined in the presence of a large number of other ions. Ta(V) and Ti(IV) can not be separated from each other. The extractable species probably has the composition 1:1:2 with respect to metal, thiocyanate and organic reagent. The conditional stepwise stability constants of the complexes have been evaluated by Yatsimirskii's and Leden's methods.

THE use of 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) for extraction and spectrophotometric determination of Cu(II) and Pd(II) has already been described by us<sup>1-3</sup>. The extraction studies of Nb(V), Ta(V) and Ti(IV) with HMMCO have now been undertaken.

HMMCO was synthesized by the method reported earlier<sup>4</sup>. A fresh solution of the reagent in chloroform was used for extraction.

Stock solutions of niobium and tantalum were prepared by fusing their oxides (AR, BDH) with potassium hydrogen sulphate and dissolving the fused mass in 20% tartaric acid. Titanium solution was prepared by dissolving potassium titanyl oxalate in dilute hydrochloric acid. The metal ion solutions were standardised gravimetrically with 8-hydroxyquinoline<sup>5</sup>. Potassium thiocyanate solution (10M) was prepared in doubly distilled water.

A Beckman DU-2 spectrophotometer with 1 cm quartz cells was used.

**Procedure** — To an aliquot of the metal ion solution was added 0.5 to 2.0 ml of 10 M potassium thiocyanate solution and enough conc. HCl to obtain 5 to 8 M acid strength in a total volume of 10 ml. The solution was shaken well with 10 ml of HMMCO solution in chloroform. After separation of the two phases, the absorbance of the organic layer was measured at 380 nm for Nb(V) and 390 nm for Ta(V) and Ti(IV). A similarly processed reagent solution was used as a blank. The amount of metal extracted was computed from appropriate calibration curve.

The Beer's law is applicable in the ranges 0.76-25.0, 3.7-108.5 and 2.93-88.0  $\mu\text{g/ml}$  in the cases of Nb(V), Ta(V) and Ti(IV). The Sandell's sensitivities for Nb(V), Ta(V) and Ti(IV) systems are 0.015, 0.072 and 0.056  $\mu\text{g/cm}^2$  respectively.

The minimum concentration of thiocyanate required for maximum extraction was found to be 0.7 M for Nb(V) and 2.0 M for Ta(V) and Ti(IV). The quantitative extraction occurs at the hydrochloric acid concentration of 8.0, 5.7 and 7.0 M for Nb(V), Ta(V) and Ti(IV) respectively and decreases thereafter. An eighty-fold excess of HMMCO for Nb(V) and Ta(V) and twenty-fold excess for Ti(IV) is sufficient for quantitative extraction.

In addition to chloroform various solvents such as benzene, toluene, hexane, cyclohexane, carbon tetrachloride, *n*-hexanol, isoamyl alcohol, isobutyl alcohol, methyl isobutyl ketone and cyclohexanone were tried. The most suitable solvent for quantitative extraction of metals was either chloroform or benzene.

The interferences of several ions in the extraction behaviour of Nb(V), Ta(V) and Ti(IV) were studied. The tolerance limit was set as the amount of foreign ion needed to cause  $\pm 2\%$  error in the recovery of metal ion. Nb(V) can be quantitatively extracted in the presence of various foreign ions. It can be separated from Ta(V) and Ti(IV) when they are added in 60- and 20-fold excesses respectively. The various ions which seriously interfere in the extraction of Ta(V) and Ti(IV) include Ce(IV), Cu(II),

TABLE 1 — STABILITY CONSTANTS OF THE COMPLEXES ( $30 \pm 1^\circ$ )

 $\{[HCl] = 8.0M (Nb), 5.7 (Ta) \text{ and } 7.0M (Ti)\}$ 

System	Method							
	Yatsimirskii			Leden			Job's	Harvey & Manning
	log $K_1$	log $K_2$	log $\beta_2$	log $K_1$	log $K_2$	log $\beta_2$	log $\beta_2$	log $\beta_2$
Nb(V)-SCN-HMMCO	2.67	2.27	4.94	2.20	2.27	4.47	4.70	4.55
Ta(V)-SCN-HMMCO	3.56	2.07	5.63	2.99	2.36	5.35	5.49	5.62
Ti(IV)-SCN-HMMCO	2.29	1.80	4.09	2.00	1.58	3.58	3.90	3.60

Fe(II), Fe(III), Nb(V),  $UO_2$  (II), V(V),  $F^-$ ,  $Mo_7O_{24}^{6-}$  and  $WO_4^{2-}$ . Ta(V) and Ti(IV) can not be separated from each other.

The relative standard deviation was  $\pm 0.50\%$ ,  $\pm 0.33\%$  and  $\pm 0.79\%$  for Nb(V), Ta(V) and Ti(IV) respectively.

The composition of the extractable species as found by various methods<sup>6-8</sup> is found to be 1:2 (metal : HMMCO). This composition is further supported by a plot of  $\log D$  (distribution ratio of the metal) versus  $\log [HMMCO]_0$  (concentration of HMMCO in organic phase at equilibrium) which gives a slope of two. Similarly, a plot of  $\log D$  versus  $\log [SCN^-]$  gives a slope of one which shows 1:1 composition with respect to metal and thiocyanate. On the basis of these observations the nature of the extractable complexes in presence of thiocyanate may be  $NbOSCNR_2$ ,  $TaOSCNR_2$  and  $TiOSCNR$ . HR (R means anion of HMMCO). It is

observed that in the case of titanium, one molecule of HR is associated through titanyl oxygen atom.

The conditional stepwise stability constants of the complexes ( $\log K_1$  and  $\log K_2$ ) have been evaluated by modified<sup>9</sup> methods of Yatsimirskii<sup>10,11</sup> and Leden<sup>12</sup>. The overall stability constants ( $\log \beta_2$ ) have been found out by Job's<sup>6</sup> and Harvey and Manning's<sup>7</sup> methods. The values obtained by various methods are given in Table 1.

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