

Spectrophotometric Determination of Ti(IV) and V(V) with 5,6, Dibromo, 2,3,4, Trihydroxyacetophenone

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ALTHOUGH a number of reagents have been reported¹⁻⁶ in the spectrophotometric analysis of titanium and vanadium there is always a search for new and better reagents. The present paper reports the application of 5,6 dibromo, 2,3,4, trihydroxyacetophenone (DBTHAP) in the spectrophotometric estimation of V(V) and Ti(IV). The proposed reagent is more sensitive than many others reported in the literature for the same purpose¹⁻⁶. The method also suffers from minimum interference from many cations and anions commonly encountered in the spectrophotometric analysis of vanadium and titanium.

DBTHAP forms an orange yellow complex with Ti(IV) (λ_{\max} 390 nm) and a green complex with V(V) (λ_{\max} 590 nm) in the pH range 3 and 5. The vanadium complex is stable for about half an hour while the titanium complex is stable for more than 12 hours. The spectrophotometric properties of the complexes are given in Table 1. Beers law

TABLE-1
SPECTROPHOTOMETRIC DATA OF Ti(IV) AND V(V)
COMPLEXES WITH DBTHAP

Metal	λ_{\max} nm	$\epsilon \times 10^3$	Sandells sensitivity $\mu\text{g}/\text{cm}^2$
Ti(IV)	390	17.5	0.0027
V(V)	590	3.5	0.0145

was studied and found to be obeyed between 0.15 and 2 ppm of titanium and 0.5 and 8 ppm of vanadium. The optimum concentration range for the effective determination as evaluated by Ringboms method was found to be 0.5 to 1.5 ppm of Ti(IV) and 3 to 6 ppm of V(V). The molar composition of the complexes determined by the Jobs method was found to be 1 : 1 in both the cases.

The effect of diverse ions was studied by adding to V(V) or Ti(IV) solutions, various cations and anions 10 times in excess. The limit of tolerance was set to $\pm 0.5\%$ deviation in the absorbance reading. It was found that ions like Cu^{2+} , Ni^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Mn^{2+} ,

Cl^- , Br^- , I^- , CH_3COO^- , ClO_4^- do not interfere, however, cations like UO_2^{2+} , Th^{4+} , Zr^{4+} and Fe^{3+} interfere seriously and should be absent.

Experimental

All chemicals used were of A.R. grade. Spectrophotometric studies were carried out on Beckman DU-2, UV-visible spectrophotometer.

Preparation of the Reagent :

The preparation of 2,3,4-trihydroxyacetophenone (THAP) was carried out by the procedure given in the literature⁷. The bromination of THAP was carried out as follows :

A cold ($\sim 10^\circ$) solution of bromine (1 g) in chloroform (20 ml) was added to a cold suspension of THAP (1.68 g) in chloroform (20 ml) and the resulting mixture was stirred for 12 hours at temperature below 10° . Pale yellow crystals were separated after the addition of petroleum ether (40-60). The product was purified by column-chromatography on silicagel using chloroform as eluent to give 5,6 dibromo, 2,3,4, trihydroxyacetophenone (DBTHAP) as pale yellow crystals. The composition of DBTHAP was verified by I. R. and elemental analysis.

Procedure :

To an aliquot containing up to 1.5 ppm of Ti(IV) or 6 ppm of V(V) was added 4 ml of $1 \times 10^{-3} M$ in case of titanium and 4 ml of $8 \times 10^{-3} M$ alcoholic solution of the reagent in case of vanadium. The pH of the mixture was adjusted to 4.5, with acetate buffer and the solution diluted to 25 ml. The absorbance readings were taken at the λ_{\max} of the complexes against the corresponding reagent blank. The amounts of the metals were calculated from the calibration curves drawn under identical conditions.

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