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Spectrophotometric Determination of Vanadium(V) with 2-Carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone

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With 8 Figures

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In our previous papers it has been reported that 2-carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone (HA) appears to be a very suitable agent for selective extraction of certain metals: niobium(V), tantalum (V) and zirconium(IV)2,3, thorium(IV) and protactinium(V)4, iron (III)5 and gallium(III)6.

Vanadium(V) can also be extracted with HA and the complex used for spectrophotometric determination. None of the other metals extracted with HA interferes. HA offers great selectivity, speed and simplicity in determination of vanadium.

Experimental

Reagents

2-Carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone was synthesized by the method described previously7 and was used in chloroform solution.

A 0.01M standard solution of vanadium(V) was made by dissolving 1.17 g of ammonium vanadate in 1 litre of distilled water and standardized gravimetrically with cupferron8. All other chemicals were of analytical grade.

Spectrophotometric Measurement at pH 1

The pH of 10 ml of solution containing 10—150 µg of V(V) is adjusted to 1 and the vanadium extracted with 5 ml of 0.005 HA in chloroform (shaking for 2 min). The organic phase is transferred
into a 10-ml volumetric flask. The aqueous phase is shaken again with 4 ml of chloroform, which is then also transferred to the volumetric flask. The extract is diluted to the mark with chloroform and the absorbance measured at 478 nm. The complex is stable for several days and Beer's law is obeyed.

**Spectrophotometric Measurement after Extraction from 4.5 M HCl**

To 1 ml of solution containing 10—150 μg of V(V) enough concentrated hydrochloric acid is added to make the final HCl concentration 4.5 M, and distilled water is added to make the total volume about 10 ml. The solution is extracted twice with 3.5-ml portions of 0.01 M HA in chloroform (shaking for 2 min). The organic phases are collected in a 10-ml volumetric flask and diluted to the mark with chloroform. The absorbance is measured at 615 nm. The complex is stable for several days and Beer's law is obeyed.

**Isolation of Extracted Vanadium(V) Species**

The vanadium(V) complexes were isolated by shaking a chloroform solution of the reagent (0.05 M) with an equal volume of ammonium vanadate solution, separating the chloroform layer and evaporating the solvent at reduced pressure. Orange VO₂A(HA)₂ was obtained at pH 1 and blue VO₂Cl(HA)₃ from 4.5 M hydrochloric acid. In both cases there was an excess of vanadium. The solid products were recrystallized from chloroform-ligroin (1 : 2) and analysed.

VO₂A(HA)₂-found: C 60.1%; H 5.3%; N 4.1%; V 5.5%.
Calculated for C₄₅H₄₄O₁₄NaV: C 59.9%; H 4.92%; N 4.66%; V 5.65%.
VO₂Cl(HA)₃-found: C 57.7%; H 5.2%; N 4.3%; V 5.3%; Cl 3.7%.
Calculated for C₄₅H₄₅O₁₄N₃VCl: C 57.60%; H 4.83%; N 4.48%; V 5.43%; Cl 3.78%.

The results for hydrogen and nitrogen in the first case, and for hydrogen in the second, are not quite within the Pregl limits of acceptability, but may be regarded as adequate within the context of the other results.

**Results and Discussion**

Vanadium(V) reacts with HA at lower acidities, regardless of the kind of mineral acid present, giving a complex which is extracted with chloroform. The orange solution has maximal absorption at 478 nm (Fig. 1). However, if the reaction is carried out in the presence of high concentrations of HCl a blue complex is obtained, but