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Short Communication

Spectrophotometric determination of molybdenum (VI)* and vanadium (V) using resacetophenone isonicotinoyl hydrazone

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Abstract

Spectrophotometric methods of estimation have been developed for the determination of molybdenum (VI) and Vanadium (V) using resacetophenone isonicotinoyl hydrazone as complexing reagent. The effect of foreign ions is also investigated.

Key words: Spectrophotometry, microamounts, molybdenum(VI), vanadium(V), resacetophenone isonicotinoyl hydrazone

1. Introduction

Resacetophenone isonicotinoylhydrazone (RPINH) is used extensively as analytical reagent[1-5]. The present paper describes the results obtained in the spectrophotometric determination of molybdenum (VI) and vanadium (V) with RPINH.

2. Experimental

Analytical grade chemicals are used in the studies. The reagent RPINH is prepared by the procedure similar to that of Sah and Peoples[6]. A stock solution (1×10^{-2}M) of the reagent in dimethylformamide is used in the solution studies. Aqueous molybdenum (VI) and vanadium (V) stock solutions (1×10^{-1}M) are prepared by dissolving respectively 6.049 g of sodium molybdate and 2.9245 g of ammonium vanadate in distilled water in 250 ml volumetric flask. The stock solutions are diluted appropriately to get the required concentrations.

The absorbance and pH measurements have been made as reported earlier[7].

Determination of molybdenum (VI): To each of a set of 25ml volumetric flasks containing 5ml of HNO_3 (0.1M) solution, 10ml of methanol, and 2ml of RPINH (1×10^{-2} M) solution an aliquot of Mo (VI) (2×10^{-4} M) solution is added and contents are made up to the mark with distilled water. After an hour the absorbance of the solution is read at 440nm against reagent blank.

Determination of vanadium (V): A procedure similar to the one as outlined above is employed using 12.5ml of buffer solution (pH 5), 2.5 ml of dimethylformamide (to avoid the precipitation of the reagent) and 2.0ml of RPINH solution (1×10^{-2} M) (total volume 25ml). The absorbance measurements are made at 410nm.

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The procedure is repeated with various aliquots of vanadium (V) and molybdenum (VI) solutions.

3. Results and discussion

RPINH reacts with molybdenum (VI) in HNO_3 medium and vanadium (V) in DMF medium in the pH range 3-6 to form yellow soluble complexes.

The absorbance of the molybdenum complex solution is found to be maximum in HNO_3 medium. The absorbance of the yellow coloured complex solution decreases gradually and therefore the addition of methanol (40% v/v) was necessary to stabilize it. The absorbance is fairly constant at an acid concentration of 0.02M even for 30 min and is maximum and constant for more than five hours at pH 5 in the V (v) complex solution. A five-fold excess of the reagent is found sufficient for maximum colour development.

Applicability of Beer's law: A linear graph is obtained between absorbance and the amount of the metal in the range 0.5 to 8.0 $\mu g.ml^{-1}$ for molybdenum and in the range 0.22 to 4.9 $\mu g\,ml^{-1}$ for vanadium. The molar absorptivity and Sandell sensitivity values for molybdenum and vanadium complexes work out respectively 0.9×10^4 lit. $mole^{-1}\,cm^{-1}$, 0.01 $\mu g\,cm^{-2}$ and 7.7×10^3 lit. $mole^{-1}$. cm^{-1}, and 0.007 $\mu g\,cm^{-2}$. The standard deviation in the absorbance for an amount of 4.8 $\mu g\,ml^{-1}$ of molybdenum (vi) is 0.005 and for 3.2 $\mu g\,ml^{-1}$ of vanadium is 0.008.

Composition and stability: The compositions (Job's continuous variation method [8]) and stability constants of molybdenum RPINH and vanadium RPINH complexes were established respectively as 1:2 (Mo:RPINH), 1:1 (V:RPINH) and 8.6×10^{11} and 8.3×10^5.

Interference studies: Various ions interfere in the determination of molybdenum. The limit of tolerance (Co^{+2}, 240; Cr^{+3}, 480; W^{+6}, Mn^{+2}, U^{+6}, Ce^{+4}, 9.6; F^-, 48; Cl^-, So_4^{-2}, ScN^{-1}, thiourea, 480; Bo_3^{-2}, PO_4^{-3}, 240; tartrate, 120) of foreign ion is taken as the amount ($\mu g\,ml^{-1}$) beyond which the change in absorbance is more than ± 2%. Copper interferes seriously but is suppressed by the addition of thiourea. In the presence of zinc and nickel the absorbance increases; it is observed that even in the presence of 100-fold excess of Zn (II) or Ni (II), the metal ion can be determined, provided a calibration curve is constructed with excess of zinc or nickel.

In the case of vanadium complex, large quantities of sodium, potassium, barium, calcium, strontium, magnesium, cadmium, tartrate, sulphate, bromide, fluoride, thiosulphate, thiocyanate, thiourea, citrate, oxalate, borate, phosphate, ascarbic acid, 25-fold excess of manganese (II), chromium (III) and two-fold excess of zinc (II) and uranium (VI) also do not interfere. But absorbance increases in the presence of zinc, cobalt, nickel, iron, chromium (VI) and aluminium (III) since they form complexes with the reagent, while in the presence of cerium and tungsten the absorbance decreases. A 100-fold excess of chromium (VI) can be masked by tartrate.

In conclusion, it may be mentioned that the present method for the determination of molybdenum (VI) offers advantages over the standard methods[9-11] since the reagent solution can be prepared easily in dimethyl formamide and is stable for weeks and can be kept in white bottles. The reagent is quite stable unlike dithiol[9,10] and the concentration of the acid and the reagent are not as critical as in the thiocyanate[11] method. Also, the present method for the determination of vanadium (V) is advantageous as almost all the existing[12] methods are extraction spectrophotometric methods. Moreover the tungstophosphovenadic acid method[12] is less sensitive ($\epsilon = 1.4 \times 10^3$ lit mole^{-1} cm^{-1}) than the present method ($\epsilon = 7.7 \times 10^3$ lit mole^{-1} cm^{-1}).

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