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Determination of Vanadium in Water and Biological Samples Using N-Hydroxy-N-*o*-Tolyl-N′-(2-Methyl)-Phenyl-Benzamidine Hydrochloride and 4-Hydroxy Benzaldehyde

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A simple rapid and sensitive method has been developed for the detection and spectrophotometric determination of vanadium(V) in water samples and biological samples. N-Hydroxy-N-*o*-tolyl-N′-2 methyl phenyl benzamidine hydrochloride reacts with vanadium(V) in presence of 4-hydroxy-benzaldehyde giving deep green-blue complex which is quantitatively extractable at pH 2.3 to 5.1. The Sandell's sensitivity of the reaction is 0.0061 $\mu g/cm^{-2}$ at 580–590 nm, with molar absorptivity 8280 ± 50 L $mole^{-1}$ cm^{-1}. Mo(V), Fe(III), Co(II) and Ni(II) etc. do not interfere with the determination. The limit of identification of the spot test based on this colour reaction is 0.1 μg of vanadium with dilution limit $1 : 1 \times 10^6$.

INTRODUCTION

The toxicity of vanadium and its compounds is considered to be similar to that of lead and mercury[1]. The toxic effects due to industrial exposure to vanadium compounds are followed by different ailments in human being such as bronchitis, pneumonia, irritation of mucous membrane, gastrointestinal and nervous disorders[1–6]. A study of Vintinner *et al.*[7] suggests that there is a direct relationship between the amount by vanadium present in the urine and the degree of exposure to metal; therefore determination of vanadium accumulated in the body tissues and blood and that excreted through urine is important for the study of toxicity of vanadium. Telvite[8] estimated vanadium in biological samples with 8-hydroxy quinoline. N-benzoyl hydroxylamine and its analogues are widely used as reagents for vanadium[9–11] but Donaldson[12] claims that low and erratic results are obtained by these methods. Several new methods for the extraction and spectrophotometric determination of vanadium(V) in steel samples have been published using mixed ligand complexes[13–18]. (N-hydroxy-N-*o*-tolyl-N′-2-methyl)-phenyl benzamidine hydrochloride (HTMPBH) has been proposed as a new reagent for reliable test of vanadium in water samples and biological samples (urine and blood). The reagent forms a green-blue complex with vanadium in presence of 4-hydroxy-benzaldehyde at 2.3 to 5.1 pH. There is no partial reduction of vanadium (V); hence quantitative extraction of the method is achieved. Some common ions including Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+} etc. do not interfere with the determination.

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EXPERIMENTAL

Absorbance measurements were made with Carl Ziess Zena Spekol spectrophotometer. pH values were determined by Systronics pH meter type 321.

All the reagents used were of analytical grade. Standard vanadium solution was prepared by dissolving ammonium metavanadate in double distilled water and standardised volumetrically[19].

HTMPBH was prepared by condensation of equimolar quantities of N-*o*-tolyl hydroxylamine and N-2-methyl phenyl benzamidoyl chloride in ether medium at 0–5°C. The white crystals of hydroxylamidine hydrochloride were crystallised from absolute ethanol. (m.p. 181°C). Analysis, found (calcd.) (%) C = 71.30, (71.48), N = 7.84, (7.94), H = 5.85, (5.95). It was used as a 0.1% solution in chloroform.

Spot test for vanadium: Two drops of vanadium solution containing 0.2 μg vanadium were placed in a micro test tube. To this added 2 to 3 drops of 4-hydroxy benzaldehyde and 1 drop 2 M HCl. Then added 0.1 mL chloroform solution of the reagent. Shake the solution for 1 min. Green-blue colour of chloroform layer confirms the presence of vanadium.

The detection limit of the method is 0.1 μg vanadium with a dilution limit of $1 : 1 \times 10^6$.

Effect of variables: The colour is stable for about 24 h at room temperature. There is no change in colour if the temperature is varied from 20–40°C. Variations in the amounts of reagent also had no effect on the stability and colour formation.

Spectrophotometric determination of vanadium (V): Vanadium solution containing 10–100 μg vanadium was taken in a separatory funnel. 2 mL of 5% chloroform solution of 4-hydroxy benzaldehyde was added. The pH of the solution was adjusted to 2.3 to 5.1 with 2 M HCl solution and 15 mL of 0.1% reagent solution in chloroform was added. The volume of aqueous phase was also kept 15 mL. The contents were shaken for 2 min. The chloroform layer was transferred in a 50 mL beaker. The aqueous phase was washed with 2×4 mL fresh portions of chloroform and the washings were mixed with the contents of the beaker and then dried over anhydrous sodium sulphate. The absorbance was measured against the reagent blank. The amounts of vanadium in the solutions were determined by comparing with standard curves.

RESULTS AND DISCUSSION

The coloured system showed maximum absorption at 580–590 nm.The molar absorptivity of the solution was found to be 8280 ± 50. l mole^{-1} cm^{-1}, at λ_{max} with Sandell's senstivity 0.0061 μg/cm^{-2}.

Effect of Variables: Benzene, toluene, carbon tetrachloride and chloroform all extract the ternary complex but chloroform was found to be most suitable for extraction work due to high solubility of the reagent and the adduct.

The acidity of the aqueous phase was adjusted with dilute hydrochloric acid. Below 2.3 and above 5.1 pH low absorbance values were obtained. Thus the optimum pH range for quantitative extraction is 2.3–5.1 pH.

8-fold and 10-fold molar excesses of HTMPBH and 4-hydroxy benzaldehyde respectively-were necessary for complete extraction of vanadium(V). A further excess of these did not affect the absorbance and λ_{max} of the mixed complex. The order of addition of the reagents was not critical.

Influence of Diverse Ions: To study the effect of foreign ions on the procedure a fixed amount of vanadium (4 ppm) was mixed with known quantity of ion under study and the pH of the solution was kept 2.3 to 5.1 and vanadium was determined according to the procedure described earlier. The inteference due to Fe^{3+} and Cu^{2+} could be eliminated by masking with trisodium phosphate and thiourea respectively (2 g), bromide, nitrate, sulphate, phosphate, borate, citrate, tartrate, urea, etc, did not interfere. The tolerance limits for other ions (in ppm) are shown in parenthesis Fe^{3+} (900)[a], Cu^{2+} (1000)[b], Mo^{6+} (300), Al^{3+} (800).

Determination of vanadium in urine/blood

Transfer 100 mL of urine/5 g of blood to a 250 mL Kjeldahl flask fitted with a loose stopper. Add to it 20 mL of concentrated nitric acid. Heat gently until foaming subsides, increase the temperature and evaporate to dryness. Cool and add 1 mL of concentrated sulphuric acid and 3 mL of concentrated nitric acid and evaporate gently to fumes. Repeat the procedure three times with addition of 3 mL aliquots of nitric acid each time.

To the ash add 2 mL of nitric acid and 25 mL of water and digest on a water bath for 30 min to hydrolyse polyphosphates to orthophosphates. Dilute the solution to 20 mL and oxidise vanadium quinquivalent state with a dilute solution of potassium permanganate at 70°C. A persistent faint pink colour indicates complete oxidation. Cool and add the solutions and washings from the Kjeldahl flask to a separatory funnel. Determine vanadium by the recommended procedure.

Tables 1 and 2 present the results of the analysis of the samples to which

TABLE-1
RECOVERY OF VANADIUM FROM WATER (100 mL) AND URINE (100 mL) SAMPLES

	Vanadium added (mg)	Recovered (mg)	Relative error (%)
Water sample	100	99.5	–0.5
	100	99.2	–0.8
	100	100.3	+0.3
	100	100.0	0.0
	100	99.1	+0.9
Urine sample	80	78.2	–2.250
	80	79.8	–2.250
	80	79.9	–0.125
	80	81.1	+1.375
	80	80.1	+0.125

The normal vanadium content of the sample was negligible.

a-In presence of trisodium phosphate.
b-In presence of thiourea.

known amounts of vanadium were added and which were then analysed according to described procedure. The results of these analyses show that vanadium can be determined with fair accuracy.

TABLE-2
RECOVERY OF VANADIUM FROM BLOOD (5 g)

Vanadium added (mg)	Recovered (mg)	Relative error (%)
100	101.0	+1.0
100	99.7	–0.3
110	110.0	0.0
110	109.0	–0.9

The normal vanadium content of the sample was negligible.

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