

Spectrophotometric Application for pH Dependent Determination of Vanadium (IV) Complexed with Thiophene-2-Carboxaldehyde Thiosemicarbazone by SPS Method

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Abstract: A new thiosemicarbazone based-sorbent matrix with sensitive selectivity and accurate spectrophotometric method was proposed for the determination of vanadium (IV) using thiophene-2-carboxaldehyde thiosemicarbazone. In our earlier paper we have reported the synthesis, complexation and analytical data of the sorbent material. It is also characterized by FAB-Mass, IR-spectra, UV-Vis spectroscopy and magnetic behaviour. In the present work we report here the advantages for using thiophene-2-carboxaldehyde thiosemicarbazone as a reagent for the spectrophotometric determination of vanadium (IV). Several extractive parameters that considered for the extraction such as pH, contact time, effect of temperature, effect of diverse ions, effect of metal ion concentration and desorption of the metal ion were studied. The results showed that the sorbent material has a special selectivity and high adsorption capacity for vanadium (IV) from aqueous samples. The quantitative recovery of V (IV) was achieved by using 1(M) EDTA solutions. The proposed method has been applied for the determination of vanadium (IV) in different water samples.

Key Words: Solid Phase Spectrophotometric (SPS), V (IV) Species, Thiophene-2-carboxaldehyde Thiosemicarbazone

I. Introduction

Vanadium is one of the abundant trace elements. Its compounds released in large quantities, mainly by burning fossil fuels and also from various alloy-steels industries [1-3]. As it has many industrial, biological and pharmacological importance. But it is an industrial hazard [4-5]. It plays an immense role in the environment for the productivity of agricultural crops [6-7]. In human body, it can bind with blood protein and increased risk of lung cancer. Pharmacological evidence suggests that vanadium plays a beneficial role in the prevention heart diseases. Recently, vanadium and its compounds came to focus in medical science due to discovery of the insulin-like and anti-cancer properties [8]. Therefore, one of the routes of vanadium incorporation into the human body in water, its determination in the samples from polluted areas, biological, geological and nutrition studies has received much interest.

Vanadium concentrations in biological and environmental samples are very low. Vanadium can be determined as the total, as well as its different oxidation species. In natural waters, dissolved exist as vanadium (IV) or vanadium (V) and these species have different toxic properties. Though, V (V) is much more toxic than V (IV), but stability experiment proved V (IV) was relatively stable for over 24 hours. It was observed that vanadium (IV) in aqueous medium forms complexes, most easily with reagent containing-N₂S₂ donor ligands [9-11]. All these above factors encouraged in the determination of vanadium (IV).

It is clear from the literature that several methods have been reported for the determination of vanadium (IV) as their chelating complexes. Few examples of chelating reagent used for complexation of vanadium are bis (Salicylaldehyde) tetramethylethylene diamine in a chloroform/water mixture, 2-hydroxyacetophenone thiosemicarbazone, salicylaldehyde acetoacetic acid hydrazone, EDTA [12-15]. All of the above complexing agents favours for the synthesis of a new thiosemicarbazone from thiophene-2-carboxaldehyde and thiosemicarbazide. A new oxovanadium complex is synthesised by a Schiff-base thiophene-2-carboxaldehyde thiosemicarbazone. The new thiosemicarbazone is considered as a selective and sensitive reagent for the spectrophotometric determination of vanadium (IV). The reported methods for the metal ions speciation and preconcentration are liquid-liquid extraction and solid phase extraction (SPE), but SPE is simpler and more convenient, because it is based on the transfer of metal ions from an aqueous phase to the active sites of a solid phase. The reported solid phases used for the determination of vanadium species include Sephadex DEAE-A-25 with Eriochrome Cyanide R complexation, C₁₈ microcolumn or XAD-7 resin with 2-(5-bromopyridylazo)-5-diethylaminophenol or dithiozone or 8-hydroxyquinoline (8-HQ), Chelex 100 [16-19]. The reported analytical methods include neutron activation analysis (NAA), inductively coupled plasma mass spectroscopy (ICP-MS), ICP-AES, electrothermal atomic absorption spectrometry (ETAAS), HPCL, spectrofluorimetry, ion chromatography and catalytic spectrophotometric. From all of the above methods, solid

phase extraction (SPE) has several advantages for its greater simplicity and efficiency [20-22]. We report here a new technique based on solid phase spectrophotometric (SPS) for the determination of vanadium (IV) complexed with thiophene-2-carboxaldehyde thiosemicarbazone (VO^{2+} -tctsc) impregnated with alumina as matrix. It is a simple, sensitive and selective spectrophotometric method is reported for the micro determination of vanadium (IV). The chelating agent is impregnated with alumina for the complexation with V (IV) ion from DMF medium. The optimum conditions for better extraction such as pH, contact time, effect of temperature, concentration metal ions, photometric studies, effect of diverse ions and elution studies were investigated.

II. Experimental

Reagents and Solutions

Extra pure methanol, ethanol, acetic acid, sodium acetate, ammonia solution and DMF, all from Sisco Research Lab., Mumbai, India were used. Vanadyl sulphate pentahydrate (BDH, India) was of analytical grade reagent, thiosemicarbazide and thiophene-2-carboxaldehyde (Sigma and Aldrich) were used for the complexation. A neutral solid sorbent alumina was of analytical reagent for the determination of the metal ion from Oxford Lab., Mumbai, India.

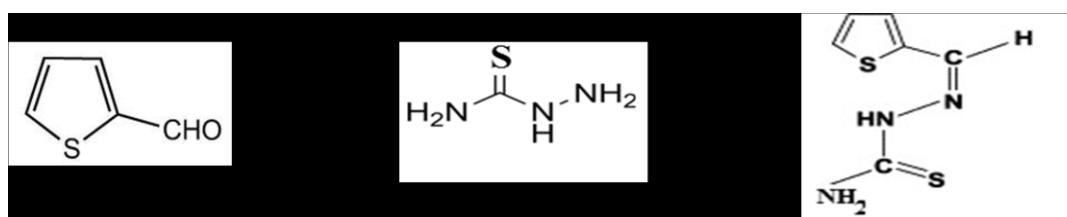
All the solutions were prepared using analytical grade reagents. A stock of 0.01M solution of vanadium (IV) was prepared by dissolving 1.989 gm of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ in doubly distilled water with adding 2 ml of 0.5 (M) H_2SO_4 because vanadium (IV) is unstable in non-acidic solution. Working solutions of vanadium (IV) were prepared by diluting appropriate volumes of stock solution with distilled water. The solution of the chelating agent was prepared in DMF. The other reagents were (0.1 M) CH_3COOH , (0.1 M) CH_3COONa and solutions of diverse ions were prepared in double distilled water.

Instrumentation

The UV-Vis spectra were recorded in DMF using Shimadzu Spectrophotometer (UV-1800). A mechanical shaker (BOD-incubator: YONA Mfg. Indian Instruments Manufacture Co., Kol-12) was used throughout the experiments. A labtronic pH meter (Model No-23) equipped with a combined glass-calomel electrode was used to monitor the pH of the solutions.

Synthesis of the Chelating Ligand (tctsc)

The transparent mixture of thiosemicarbazide (1mmol) in acetic acid at 50°C , was added drop wise freshly distilled thiophene-2-carboxaldehyde (1 mmol) for 5 minutes. The reaction mixture was stirred for another 30 minutes at 50°C . The yield of the reaction mixture was cooled down and washed with water (20 ml) and pure ethanol (20 ml) and finally dried at $70\text{-}80^\circ\text{C}$ for at least 5 hours. The greenish yellow yield of 89.2% was heated in an oven at 80°C and finally crystallized from hot ethanol. Anal. Calcd for $\text{C}_6\text{H}_7\text{N}_3\text{S}_2$ (185 g/mol), m.p. 240.2°C , C, 38.91, N, 22.70, S, 34.59, H, 3.78% Found: C, 38.90, N, 22.71, S, 34.61, H, 3.80%. FAB-Mass: m/z, 185.1 (M^+). IR: 1735 cm^{-1} , ν (C=O), 3315 cm^{-1} , ν (NH_2), $1612\text{-}1633\text{ cm}^{-1}$, ν (HC=N). UV-Vis: 433-344 nm and 281-258 nm.



Preparation of tctsc-Sorbent

Impregnation of 1g thiophene-2-carboxaldehyde thiosemicarbazone on the surface of 3.0 g of alumina was prepared at the ratio of 1:2 in methanol solvent to the following procedure [23-24]. A 1×10^{-2} M of tctsc which has been dissolved in DMF was added to the sol solution and stirred for 40 minutes at room temperature. The resulting homogeneous composition was left in an oven at 60°C for one day. After drying, the sorbent was ground into powdered for metal ion extraction. Blank sorbent was prepared by the same procedure.

General Procedure

For the batch method of extraction 200 mg of sorbents were taken in each of 100 ml flasks with 20 ml of 0.5 mg of V (IV) and 1 ml of DMF was added in each sets and the pH was adjusted to 5.5 using dil. HCl and liquid ammonia solutions. The mixtures were shaken by a mechanical shaker at about 400-500 rpm at room temperature (35°C) for 1h. After the extraction, the filtrates and unextracted V (IV) were determined by UV-Vis spectrophotometer at λ_{max} 450 nm. The concentration of V (IV) adsorbed on the sorbent materials was calculated by the difference. The different experimental parameters such as pH, equilibrium time, effect of temperature,

effect of diverse ions, concentration of eluents and photometric methods were studied to optimize the sorption of the metal ion.

III. Results and Discussion

The nature and properties of the sorbent used in SPS is very important for the determination of vanadium, because this metal exists in different oxidation states as well as many complex species. Vanadium (IV) exists as vanadyl cation VO^{2+} , which is stable in acidic conditions. In order to select the appropriate sorbent for the extraction of vanadium (IV) in acidic condition, thiophene-2-carboxaldehyde thiosemicarbazone is one of the acidic chelating agents. In this proposed method we used tctsc as an extracting agent for the selective solid phase determination of V (IV) ions by tctsc-alumina beads and spectroscopy. The absorption spectra of these greenish yellow coloured complex solutions show maximum at 450 nm and the calibration graph was constructed.

Effect of pH

The influence of pH for the percentage of extraction was investigated at a pH range 2.1 to 7. The extraction of metal ion was done with 200 mg of chelating matrix in DMF. The unextracted V (IV) ion concentration was calculated from the supernatant solution of V (IV) ion by UV-Vis spectrophotometric method. The results showed in [Fig.1], that the percentage of metal ion uptake increases up to the pH 5.5. As it can be seen that at high pH, leads to decrease in the retention of V (IV) due to the unstability in non-acidic solution. Hence, pH=5.5 was chosen for further studies of V (IV) ion.

Effect of Temperature

The influence of the temperature on the percentage of extraction of 0.5 mg/ml of V (IV) was studied in the temperature range of 20-55^o C at pH 5.5. The results showed in [Fig.2], that the percentage of sorption of the metal ion increases with temperature. It is found maximum sorption at 35^o C and then decreases after the optimum temperature. Hence, the simplicity of temperature control throughout the extraction, a temperature of 35^o C was chosen for further studies.

Kinetic Study

The effect of control time required during the metal ion extraction is considered. In this regard, the extraction was carried out by the sorbent matrix with V (IV) ion at the optimum conditions from 30 to 300 min. and the respective results are presented in [Fig.3]. It can be seen that over 75% of V (IV) was extraction within 90 min. Increase of control time, sorption equilibrium of the metal ion reached after the maximum quantity of sorption. Therefore, 90 min extraction time was chosen for subsequent studies.

Effect of Reagent (tctsc) Concentration

The influence of the concentration of the reagent impregnated with alumina in solid sorbent matrix was studied in the range of 1×10^{-2} to 1×10^{-6} M. It was found that the presence of less amount of the reagent decreases in the sorption of V (IV) ion which is shown in [Fig.4]. The high efficiency of the reagent is more than 80% at 1×10^{-2} M. But beyond this range of the reagent concentration does not influence on the extraction of V (IV) ion.

Effect of V (IV) ion concentration

At a fixed tctsc concentration (1×10^{-2}) in the solid matrix, the adherence to Beer's law was studied by measuring the absorbance of the series of solution containing different concentrations of V (IV). A linear calibration graph is constructed between absorbance and metal ion concentration predicts that V (IV) may be determined in the range of 0.1 to 0.5 mg/ml. The molar absorptivity is 1.63×10^2 L mol⁻¹ cm⁻¹. The calibration graph is shown in [Fig.5].

The influence of the concentration on the extraction efficiency was investigated by the different concentrations of V (IV) ion with 200 mg of the solid sorbent matrix at pH 5.5. It can be seen [Table 1] that over 75% of V (IV) was extracted in the above series of solution range (0.1 to 0.5 mg/ml). It was also found that high efficiency of the sorbent towards V (IV) ion at high concentration.

Effect of Diverse ions

The effect of interfering ions is examined for their effect on the determination of vanadium (IV) ion. The tolerance limit (in mg) of these ions in the determination of 0.5 mg/ml of vanadium (IV) ions is within a relative error of $\pm 2\%$. The results are given in [Table 2]. It can be concluded that the proposed is highly selective because various cations and anions can be tolerated at efficiency levels.

Desorption Studies of V (IV) ion

The selection of a suitable eluent for desorption of vanadium (IV) ion is one of the important factors to obtain efficiency of the resin and recovery of the metal ion. Low absorption of metal ions at low pH helps to considered acidic eluent of hydrochloric acid, nitric acid, sulphuric acid, oxalic acid, thiourea and EDTA. Finally, it can be seen from [Table 3], the best results were obtained by using 1mol L⁻¹ EDTA solution. Various volumes of 1mol L⁻¹ EDTA solutions were used for desorption of V (IV) ion and extraction efficiency is found to increase by increasing their volumes. The quantitative recovery was studied by using 5 ml, 10 ml, 15 ml and 20 ml of 1mol L⁻¹ EDTA for V (IV) ion.

Application

In order to confirm the application of the proposed method at optimum conditions was applied for the determination of V (IV) in tap water, river water, well water, mineral water and waste water. The results are summarised in [Table 4] and showed that the recovery of V (IV) is satisfactory.

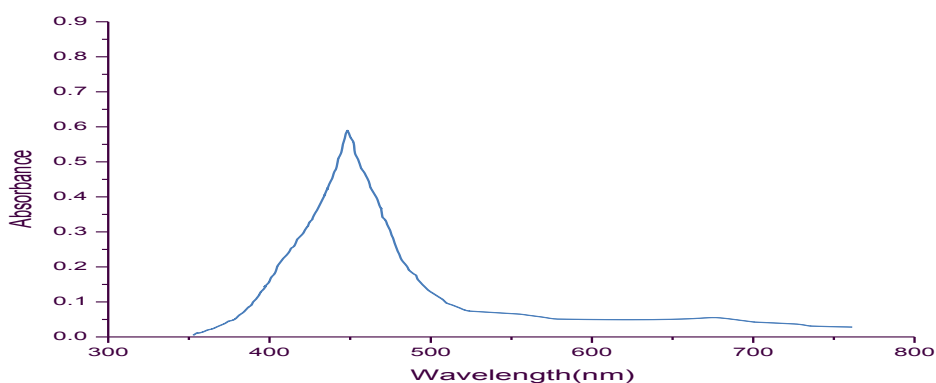


Fig.1: Absorption Spectra of V (IV)-tctsc Complex

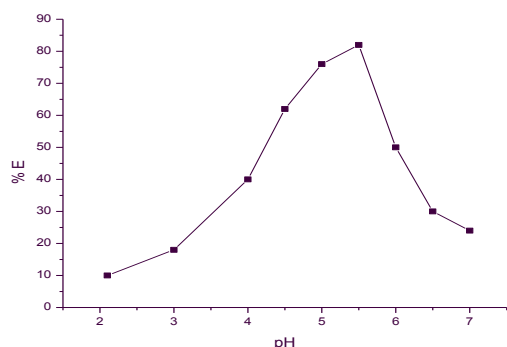


Fig.2: Effect of pH on the extraction of 0.5 mg/ml V (IV) ion.

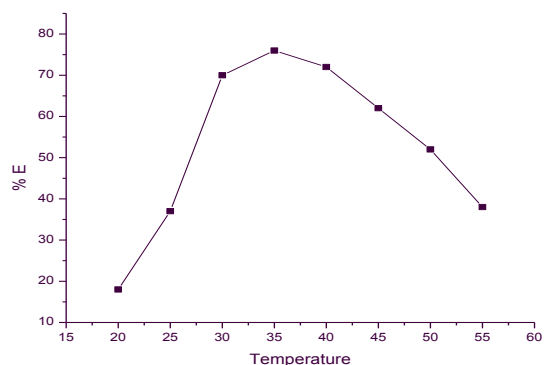


Fig.3: Effect of temperature on the extraction of 0.5 mg/ml V (IV) ion.

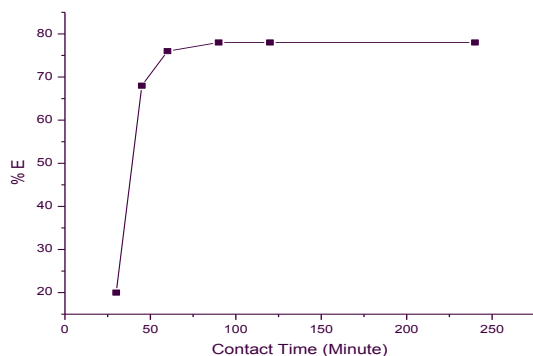


Fig.4: Effect of contact time on the extraction of V (IV) ion.

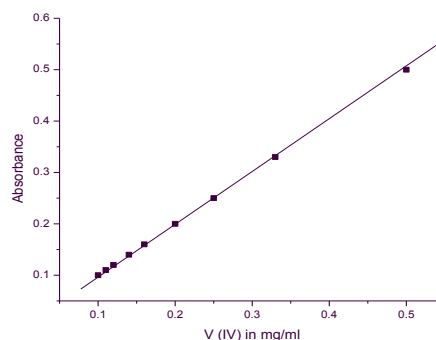


Fig.5: Effect of the reagent (tctsc) on the extraction of V (IV) ion.

Table-1 Effect of V (IV) ion concentration on the extraction efficiency of the impregnated ligand with alumina.

Used (mg/ml)	Extracted (mg/ml)	% E	Capacity of the sorbent (mmol g ⁻¹)	% RSD
0.1	0.08	72.7	9.8x10 ⁻⁶	0.19
0.11	0.08	72.7	9.8x10 ⁻⁶	0.19
0.12	0.08	72.7	9.8x10 ⁻⁶	0.19
0.14	0.1	71.4	1.0x10 ⁻⁵	0.2
0.16	0.11	68.7	1.07x10 ⁻⁵	0.09
0.2	0.14	70	1.37x10 ⁻⁵	0.18
0.25	0.18	72	1.76x10 ⁻⁵	0.17
0.33	0.24	72	2.37x10 ⁻⁵	0.15
0.55	0.38	76	3.73x10 ⁻⁵	0.1

Table-2 Effect of Diverse ions on the extraction of V (IV) ion by impregnated ligand (tctsc)

Ions	Tolerance limits (mg/ml)	Ions	Tolerance limits (mg/ml)
Mg ²⁺	100	Cl ⁻	210
Na ⁺	90	Br ⁻	150
K ⁺	87	C ₂ O ₄ ²⁻	120
Ca ²⁺	86	NO ₃ ⁻	87
Cu ²⁺	85	F ⁻	70
Ni ²⁺	75	SCN ⁻	56
Ba ²⁺	70	Thiourea	50
Fe ³⁺	69	PO ₄ ³⁻	49
Pb ²⁺	62	CH ₃ COO ⁻	35
Zn ²⁺	50	SO ₄ ²⁻	20

Table-3 Desorption studies of vanadium (IV) ion by different eluents.

Eluent Composition	% Recovery	% RSD
HCl	1 mol L ⁻¹	55.4
	2 mol L ⁻¹	60.2
HNO ₃	1 mol L ⁻¹	65.1
	2 mol L ⁻¹	71.2
H ₂ SO ₄	1 mol L ⁻¹	59.1
	2 mol L ⁻¹	62.1
Oxalic Acid	1 mol L ⁻¹	40.5
Thiourea	1 mol L ⁻¹	42
EDTA	1 mol L ⁻¹	95.6

Table-4 Determination of vanadium (IV) in different water samples by the proposed method.

Sample	Amount of V (IV) ion mg/ml		Recovery (%)
	Added	Found	
Tap Water	0.5	0.46	92
	0.33	0.3	90.9
River Water	0.5	0.44	88
	0.33	0.29	87.87
Well Water	0.5	0.47	94
	0.33	0.31	93.93
Mineral Water	0.5	0.452	90.4
	0.33	0.31	94.54
Waste Water	0.5	0.48	96
	0.33	0.302	91.5

IV. Conclusion

The proposed spectrophotometric method for the determination of V (IV) ion is simple, sensitive and selective. This method is based on the immobilization of thiophene-2-carboxaldehyde thiosemicarbazone (tctsc) on alumina. Because, it contains hard donor-N₂S₂ sites for binding of V (IV) ion. The method showed minimum interferences with diverse ions and recovery of V (IV) was quantitative. It is evident in the proposed method that thiophene-2-carboxaldehyde thiosemicarbazone (tctsc) is most sensitive thiosemicarbazone for the spectrophotometric determination of vanadium (IV).

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