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## *N*-*p*-Chlorophenyl-2-thenohydroxamic Acid a Sensitive Reagent for Spectrophotometric Determination of Vanadium\*

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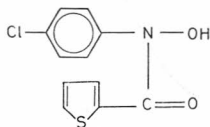
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The solvent extraction and spectrophotometric determination of vanadium(V) with *N*-*p*-chlorophenyl-2-thenohydroxamic acid (CPTHA) is described. The absorption spectrum of the vanadium(V)-CPTHA extracts in chloroform, from 4 mol/dm<sup>3</sup> hydrochloric acid has its absorbance maximum at 530 nm; the reagent being colourless does not absorb at this wavelength. The coloured system obeys Beer's law over a wide range. The molar absorptivity in terms of vanadium is 5500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at 530 nm. The optimum acid range for quantitative extraction of the chelate is 3 to 9 mol/dm<sup>3</sup> hydrochloric acid. The method is free from the interference of iron(III) and several other alloying elements which are often associated with vanadium. The method has been successfully used for determination of vanadium in BCS steels.

### INTRODUCTION

The procedure reported by this research group<sup>1,2</sup> and Ryan<sup>3</sup> for the spectrophotometric determination of vanadium(V) using PBHA is widely recognised as a major development in the quantitative analysis of microgram quantities of vanadium(V). Later on scientific workers from all over the world have been prompted to examine several analogues of PBHA in the hope of developing superior reagents for vanadium(V).

In view of the earlier findings of the beneficial influence of the thiophene ring on the coordinating properties of reactive groups<sup>4,5</sup> and improved stability of the resulting compounds *N*-*p*-chlorophenyl-2-thenohydroxamic acid (CPTHA),



was examined for the spectrophotometric determination of vanadium in concentrated hydrochloric acid media. It forms a violet complex with vanadium(V) which is extracted in chloroform. The chloroform extracts show a broad absorption band around 530 nm at all levels of vanadium concentrations. The reagent does not absorb at this wavelength. The system obeys Beer's law. The molar absorptivity of the complex was found to be 5500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. It

\* Part of Ph. D. Thesis (Ravishankar University, Raipur) 1977 by R. P.

tolerates Ce(IV), Ti(IV), Zr(IV) and Mo(VI) in large amounts which seriously interfere with other procedures for determination of vanadium(V) with hydroxamic acid.

#### EXPERIMENTAL

##### Apparatus

Visible absorption spectra were obtained on SPECORD, Carl Zeiss, Jena automatic recording spectrophotometer, using 10-mm matched silica cells. Fixed wavelength measurements were made on Electronic Corporation of India, Hyderabad, model GS 865 spectrophotometer. Graduated apparatus of standard calibration were used for all quantitative measurements.

##### Reagents

*N-p-Chlorophenyl-2-thenohydroxamic Acid.* — The method of its preparation is reported elsewhere<sup>6</sup>. 0.1% w./v. solution of CPTHA in ethyl alcohol free chloroform was used for all extraction work.

*Ammonium metavanadate.* — A. R. ammonium metavanadate was dissolved in glass distilled water. For conversion of any vanadium(IV) to vanadium(V) potassium permanganate in presence of sulphuric acid, perchloric acid or bromine water were found to be satisfactory. Vanadium content of the solution was determined volumetrically<sup>7</sup>.

*Diverse ions.* — The solutions of various ions were prepared from A. R. grade salts following the procedure of West<sup>8</sup>.

*Ethyl alcohol free chloroform.* — Ethyl alcohol was removed by washing chloroform four or five times with distilled water. It was dried over fused calcium chloride, distilled and used.

*Colour reaction* — Chloroform solution of CPTHA gives intensely purple extracts with vanadium(V) from solutions which are more concentrated than 2 mol/dm<sup>3</sup> in hydrochloric acid. The extracts gradually changed their hue from purple to reddish purple to brown as the hydrochloric acid concentration of the aqueous phase is gradually reduced to zero. All the coloured systems have broad absorption band. These are shown in Figure 1. and data therefrom are summarised in Table I. The extracts obtained in weakly acidic media are unsuitable for quantitative studies.

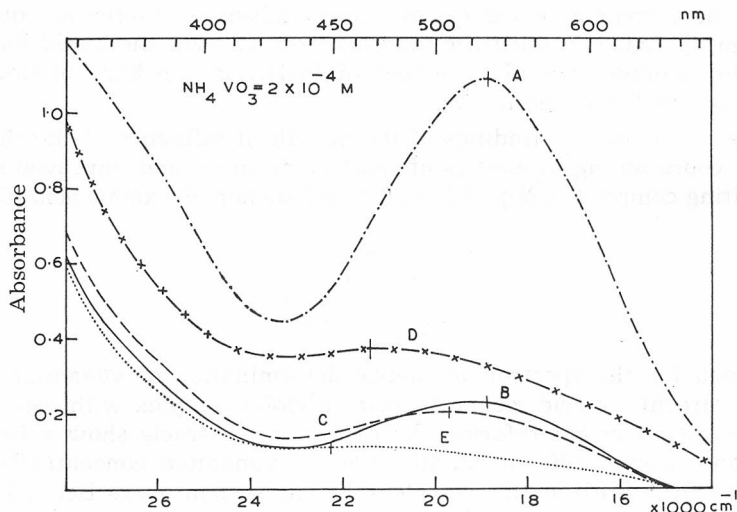


Figure 1. — Absorption spectra of vanadium(V) — CPTHA coloured extracts in chloroform · HCl in aqueous phase, (A) 4M (B) 2M (C) 1M (D) 0.1M and (E) NII.

TABLE I

*Spectral Characteristics of Vanadium(V)-CPTHA Coloured Systems in Chloroform*

Aqueous Phase, HCl mol/dm <sup>3</sup>	Colour of Chloroform Extract	Absorption band nm	Molar Absorptivity
4.0	Purple	530	5,500
2.0	Purple	530	*
1.0	Reddish Purple	505	*
0.1	Brown	465	1,800
Nil	Brown	445	*

\* Extraction is not quantitative.

*Procedure for colour development.* — An aliquot of vanadium(V) solution containing 20 to 200  $\mu\text{g}$  of metal was transferred to a separatory funnel and added concentrated hydrochloric acid was adjusted to adjust the acidity in the range 3 to 9 mol/dm<sup>3</sup>. 10 to 15 ml of reagent solution was added and the colour in the organic phase was extracted. The two phases were separated and the coloured chloroform extract after drying over anhydrous sodium sulphate was transferred to a 25 ml volumetric flask. The aqueous phase was again shaken with 2 to 5 ml of the reagent solution to ensure complete extraction of vanadium(V). The colour of the aqueous layer was wash out completely with 3 to 4 ml portions of chloroform. The washings were combined with the main extracts and the volume was made up to mark. The aqueous phase was evaporated to dryness and tested for any vanadium by spot test<sup>9</sup>.

## DISCUSSION

*N-p-Chlorophenyl-2-thenohydroxamic acid* is a white crystalline stable solid. Its solution in chloroform is colourless and shows no absorption in visible region. Its solubility in water and chloroform at 25 °C is 0.016 and 4.60 grams per liter, respectively. The distribution ratio of CPTHA between chloroform and water is  $215 \pm 5$  at 25 °C.

*Effect of Variables*

The effects of several experimental variables on the colour development were examined. Studies were made at several levels of vanadium concentrations but in the following tables only typical results only are presented.

*Acidity*

Maximum colour develops in the range from 3 to 9 mol/dm<sup>3</sup> HCl. Generally, the measurements were made from solutions which were 4 mol/dm<sup>3</sup> in hydrochloric acid.

A few workers reported<sup>10,11</sup> the reduction of vanadium(V) to vanadium(IV) in concentrated hydrochloric acid solution. Experiments carried out in this direction showed that at 30 °C up to an 6 mol/dm<sup>3</sup> HCl concentration the reduction of vanadium(V) to vanadium(IV) was less than 0.5% in six hours. In 8 mol/dm<sup>3</sup> HCl it was about 1% in two hours. The rate of reduction of vana-

dium(V) was, however, faster if the aqueous saturated solution of hydroxamic acid was also added to the reaction mixture containing ammonium metavanadate and hydrochloric acid. No quantitative data were obtained on this problem. From these studies it is inferred that the reduction of vanadium(V) to vanadium(IV) is negligible if the recommended procedure for colour development is followed. The distribution ratio of the complex between chloroform and aqueous phase is large and the complex formation reaction is also fast. Hence, the vanadium(V)-CPTHA complex passes into the organic phase rapidly and is thus protected.

#### *Amount of Reagent*

For maximum colour development 8 moles of ligand are needed for each mole of vanadium. In practice, for 0.1 mg of vanadium 10 mg of CPTHA dissolved in 10 ml chloroform were used.

The order of addition of reagents is not critical. The colour is extracted from the aqueous phase in the chloroform layer in less than one minute. The coloured extracts are stable for several days if stored in an cool dark place. Normal variations in room temperature from 15 to 40 °C did not produce any measurable change in the absorbance of chloroform extracts.

#### *Solvents for Extraction*

The most efficient solvents are chloroform and *o*-dichlorobenzene. TBP and mesityl oxide are unsuitable because the former reduces vanadium(V) to vanadium(IV) whereas the latter produces a yellow colouration with the ligand. Water-immiscible higher alcohols such as *n*-hexanol, *n*-octanol and dodecanols either did not extract the colour or imparted a red colour to them.

#### *Extraction of Vanadium(V)-CPTHA Complex in Different Acids*

Extraction of the vanadium(V)-CPTHA complex in sulphuric or acetic acid media gave brown and red extracts, respectively. These are unstable hence unsuitable for colorimetric determination of vanadium(V). Nitric and hydrobromic acids are also unsuitable for adjusting the acidity because the former oxidises the reagent whereas the latter reduces vanadium(V) to vanadium(IV). In a perchloric acid medium reddish-violet extracts were obtained.

Extracts obtained in different acids media when shaken with 4N or more concentrated hydrochloric acid turn violet and are stable and indential in all respects with those violet extracts which are obtained directly from hydrochloric acid media.

#### *Beer's Law and Precision Studies*

The optimum range for determining vanadium and the sensitivity of the reaction based on Sandell's recommendations, works out to be 2 to 7 µg per ml vanadium and 0.009 µg of vanadium per sq. cm at 530 nm, respectively. Standard deviation of 10 repetitive analyses of the same sample in terms of absorbance ins 0.006 while relative standard deviation is 1.67%.

*Interference Studies*

The desired diverse ion was added to the system before introducing the reagent solution. The recommended procedure for colour development was not altered except when a precipitate formed or an interference was minimised by adding some masking agents. An interference was caused when (i) the hue of the extract changed and, therefore, the absorption band registered a shift from 530 nm and (ii) absorbance obtained fell  $\pm 26$  from the average value. Al(III), Ba(II), Bi(III), Cd(II), Ce(IV), Co(II), Cr(III), Cu(II), Fe(III), Li(I), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV), UO<sub>2</sub>(II), Zn(II), chloride, acetate, perchlorate, nitrate, phosphate and sulphate did not interfere with the determination of vanadium even when the weight ratio of each of these ions to vanadium was as high as 225 to 1. The system tolerates fairly large amounts of Ti(IV), Zr(IV) and molybdate (Table II). Strong oxidising agents produce yellow or brown extracts, but these can be suitably reduced to non-interfering species. Reducing agents will obviously interfere in the determination of vanadium and are oxidised during the oxidation step preceding colour development.

TABLE II  
Effect of Diverse Ions

(Vanadium(V) Concentration = 84  $\mu\text{g}/25$  ml, HCl = 4 mol/dm<sup>3</sup>)

Ion	Added as	Amount of Ion Added mg	Relative Deviation %
I	II	III	IV
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	20	0
Ba <sup>2+</sup>	Ba(NO <sub>3</sub> ) <sub>2</sub>	100	+1.4
Bi <sup>3+</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	20	-1.4
Ce <sup>4+</sup>	Ce(SO <sub>4</sub> ) <sub>2</sub>	100	+2.8
Cd <sup>2+</sup>	3CdSO <sub>4</sub> ·8H <sub>2</sub> O	100	+1.4
Co <sup>2+</sup>	CoSO <sub>4</sub> ·7H <sub>2</sub> O	100	0
Cr <sup>3+</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub>	20	-1.4
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	20	-1.4
Fe <sup>3+</sup>	FeCl <sub>3</sub>	20	-1.4
Li <sup>+</sup>	Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	100	+2.8
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	100	+1.4
Mn <sup>2+</sup>	Mn(NO <sub>3</sub> ) <sub>2</sub>	20	+1.4
MoO <sub>4</sub> <sup>2-</sup>	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	10	-1.4
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	80	+1.4
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	100	0
Th <sup>4+</sup>	Th(NO <sub>3</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	20	0
Ti <sup>4+</sup>	K <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	10	0
Tl <sup>+</sup>	Tl <sub>2</sub> CO <sub>3</sub>	20	-4.2
UO <sub>2</sub> <sup>2+</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	20	-1.4
WO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	10	-4.2
Zn <sup>2+</sup>	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	100	0
Zr <sup>4+</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub>	3	0
CH <sub>3</sub> COO <sup>-</sup>	CH <sub>3</sub> COOH	3.0 mol/dm <sup>3</sup>	+2.8
ClO <sub>4</sub> <sup>-</sup>	HClO <sub>4</sub>	1.5 mol/dm <sup>3</sup>	0
NO <sub>3</sub> <sup>-</sup>	HNO <sub>3</sub>	0.02 mol/dm <sup>3</sup>	+2.8
PO <sub>3</sub> <sup>3-</sup>	H <sub>3</sub> PO <sub>4</sub>	0.5 mol/dm <sup>3</sup>	+2.8
SO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> SO <sub>4</sub>	0.8 mol/dm <sup>3</sup>	+2.8

Ions such as Ag(I), Hg(II), Pb(II), Tl(I) and tungstate which yield precipitates with HCl can cause interference. Removal of precipitate by filtration or centrifugation and extraction of the adsorbed vanadium by repeatedly shaking the precipitate with hydrochloric acid and CPTHA solution generally succeeded. Lead did not interfere if the aqueous phase was suitably diluted. Masking agents such as EDTA and phosphoric acid when present in large quantities interfere because of the competitive complexation reaction.

### B.C.S. Steels

The procedure for dissolution the steel is due to Scott<sup>12</sup>, and the solution was used directly for determining vanadium following the recommended procedure.

The results obtained in the analysis of B.C.S. steels and presented in Table III are in excellent agreement with the certified values. This establishes the reliability and accuracy of the newly developed method. Another interesting feature of the method is that unlike other spectrophotometric methods for vanadium(V), which involve prior separation of iron and other alloying metals by precipitation, ion exchange or electrolysis at the mercury cathode,<sup>13,14</sup> this method determines vanadium directly. It is thus simple and rapid also.

TABLE III  
Determination of Vanadium in B.C.S. Steels

No.	B.C.S. Steel	% of Vanadium	
		Certified	Found
252	Low Alloy	0.46 <sub>0</sub>	0.459
224	Cr-V Steel	0.24 <sub>2</sub>	0.240

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**SAŽETAK*****N-p*-klorofenil-2-tiofenhidroksamna kiselina, osjetljiv reagens za spektrofotometrijska određivanje vanadija**

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Opisan je postupak za određivanje vanadija(V) koji se temelji na ekstrakciji i spektrofotometrijskom mjerenju obojenja kompleksa s *N-p*-klorofenil-2-tiofenhidroksamnom kiselinom. Reagens je bezbojan, a za kompleks ekstrahiran iz solno-kisele otopine u kloroform karakterističan je apsorpcijski maksimum kod 530 nm [ $\epsilon = 5500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \text{ V(V)}$ ]. Ekstrakcija je kvantitativna iz otopine koja je 4—9 mol/dm<sup>3</sup> s obzirom na solnu kiselinu. Valjanost Beerova zakona provjerena je u širokom rasponu koncentracija vanadija.

Postupak je uspješno primijenjen za određivanje vanadija u čelicima, a postoje i daljnje mogućnosti primjene, jer željezo(III) i elementi koji se često nalaze uz vanadij u slitinama ne predstavljaju smetnju.

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