

CCA-1165

YU ISSN 0011-1643

541.121:546.881

Original Scientific Paper

***N*-Hydroxy-*N*-*p*-chlorophenyl-*N*'-(3-chloro-4-methyl)-phenyl-*p*-toluamidine as a New Sensitive and Selective Chromogenic Reagent for Extractive Photometric Determination of Vanadium(V) in Presence of Phenol, *p*-Chlorophenol or 2-Naphthol**

R. S. Kharsan and R. K. Mishra

Chemistry Department, Ravishankar University of Raipur, Raipur 492 002 India

Received November 27, 1978

A new method for the extraction and spectrophotometric determination of vanadium(V) using *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-(3-chloro-4-methyl)phenyl-*p*-toluamidine (HCPCMPTA) in the presence of phenols is proposed. The complexes, which can be quantitatively extracted into chloroform, show  $\lambda$  max at 595—625 nm having a molar absorptivity in the range 6000—7600 l mole<sup>-1</sup> cm<sup>-1</sup>. Many ions commonly associated with vanadium(V) such as Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, W<sup>6+</sup>, Mo<sup>6+</sup>, Mn<sup>2+</sup>, Nb<sup>5+</sup> and Ta<sup>5+</sup> do not interfere. The method has been applied for the determination of vanadium in standard steel samples.

The synergic extraction of vanadium(V) using a monoprotic and bidentate chelating agent<sup>1-4</sup> in the presence of an anion such as thiocyanate, azide etc. or an adduct-forming substance such as carboxylic acid or phenol<sup>5-9</sup>, is of considerable interest. Such complexes are very stable in organic solvent and can be used for spectrophotometric determination of vanadium content of alloy steels<sup>10</sup> and for the atomic absorption spectrometric determination of vanadium<sup>11</sup>. *N*-Hydroxy-*N,N*'-diarylbenzamidines<sup>12,13</sup>, the recently explored class of reagents possessing monobasic and bidentate hydroxyamidine functional grouping have very recently been used as chromogenic<sup>14-18</sup> and gravimetric<sup>19-22</sup> reagents for several metal ions. The present paper reports the use of a newly synthesised reagent *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-(3-chloro-4-methyl)phenyl-*p*-toluamidine (HCPCMPTA) for the extractive photometric determination of vanadium(V). The proposed method based on the chloroform extraction of vanadium(V) as V-HCPCMPTA-PhOH complex and its subsequent spectrophotometric determination is rapid and better in sensitivity than the method reported by Kojima et al<sup>9</sup> and Rao et al<sup>10</sup> which use the vanadium(V)-8-quinolinol-PhOH/anion system. A distinct advantage of the present very selective method unlike the method of Kojima et al., is that the molar absorptivity of the vanadium adducts do not increase even if the phenol concentration is increased above optimal concentration. The utility of the proposed method has been confirmed by analysing the vanadium content of some standard steel samples.

## EXPERIMENTAL METHODS

*Apparatus*

A Carl-Zeiss specord recording ultraviolet spectrophotometer and an ECIL UV-VIS spectrophotometer model GS-865 equipped with 1-cm matched silica and quartz cells were used for all photometric measurements. The pH values were determined by a Systronic pH meter type-322.

*Reagents*

*N*-Hydroxy-*N*-*p*-chlorophenyl-*N'*-(3-chloro-4-methyl)phenyl-*p*-toluamidine was synthesised by coupling equimolar quantities of *N*-(3-chloro-4-methyl)phenyl-*p*-toluimidoyl chloride and *N*-*p*-chlorophenyl hydroxylamine in ether medium<sup>12,13</sup> at low temperature. The resulting hydrochloride was treated with dilute ammonia to liberate the corresponding free base. The free base was crystallised from benzene: petroleum ether (2 : 1); m. p. 156 °C, Yield 72%.

*Anal.* C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>OCl<sub>2</sub> calc'd.: C 65.45; H 4.67; N 7.27%  
found: C 65.12; H 4.38; N 6.98%

A 0.1% (w/v) reagent solution and a 0.2 mol/dm<sup>3</sup> solution of phenols were prepared in chloroform and used for extraction.

A stock solution of vanadium(V) was prepared by dissolving AnalaR ammonium-metavanadate in glass-distilled water. Vanadium content of the solution was determined volumetrically<sup>23</sup>. All the chemicals and reagents used were of BDH the AnalaR grade.

*Procedure*

Place an aliquot (5–10 ml) containing 100 μg of vanadium(V) in a 100-ml separatory funnel and adjust the acidity required (Table I) with glacial acetic acid to a total volume of 25 ml. Shake for 1 min with 5 ml reagent solution and 5 ml phenol solution. Allow the phases to separate and transfer the chloroform layer into a 50-ml beaker containing 2 g of anhydrous sodium sulfate. Wash the aqueous

TABLE I

*Spectral Characteristics of Vanadium-HCPCMPA Complexes with Phenol, -p-Chlorophenol or 2-Naphthol in Chloroform*

Characteristics	phenol	<i>p</i> -chloro-phenol	2-naphthol
Acidity range	0–6.0	0–5.5	0–5.0
Acetic acid, mol/dm <sup>3</sup>			
Optimum conc. ranges on the basis of Beer's law ppm of V in CHCl <sub>3</sub>	0.7–7.8	0.6–7.0	0.45–6.0
Optimum conc. ranges on the basis of Ringbom plot, ppm of V in CHCl <sub>3</sub>	1.0–7.0	0.8–6.2	0.6–5.5
colour	DB	DB	BG
λ max nm	595	595	625
ε, l mol <sup>-1</sup> cm <sup>-1</sup>	6000	7000	7600
Sandell's sensitivity μg/cm <sup>2</sup>	0.0085	0.0072	0.0067

DB = deep-blue; BG = bluish-green

phase twice with 3 ml portions of chloroform. Dilute the combined extracts to a final volume of 25 ml with chloroform. Measure the absorbance at  $\lambda$  max against chloroform as a blank.

## RESULTS AND DISCUSSION

*Absorption Spectra*

The absorption spectra of vanadium-HCPCMPTA complex in absence and presence of phenols are shown in Figure 1. The reagent shows negligible absorption in the region 450—700 nm. The vanadium-HCPCMPTA complex in absence of phenols (at pH 3.0) show a flat  $\lambda$  max in the region 560—580 nm with  $\epsilon$ , 1700 l mol<sup>-1</sup> cm<sup>-1</sup>. However, a strong hyper- and bathochromic effect of adduct in chloroform solution is observed in the presence of phenols as shown in Table I and Figure 1.

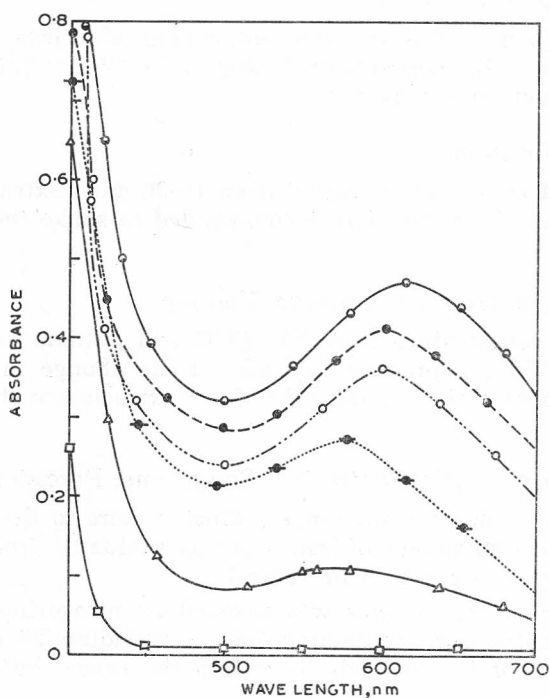


Figure 1 Absorption Spectra

- $6.28 \times 10^{-5} C_v + \text{HCPCMPTA} + 2\text{-naphthol}$
- $5.88 \times 10^{-5} C_v + \text{HCPCMPTA} + p\text{-chlorophenol}$
- $6.11 \times 10^{-5} C_v + \text{HCPCMPTA} + \text{phenol}$
- $5.88 \times 10^{-5} C_v + \text{HCPCMPTA} + \text{Acetic acid}$
- $6.28 \times 10^{-5} C_v + \text{HCPCMPTA}$
- 0.003 M HCPCMPTA

*Effect of Experimental Variables*

Various organic solvents like benzene, toluene, carbon tetrachloride, chloroform etc. were tried for extracting the vanadium complexes. Chloroform was chosen because of the free solubility of reagent in it and its high extractability towards the ternary complexes.

### *Effect of Acidity*

The acidity of the aqueous phase for extraction of ternary complexes was maintained with glacial acetic acid and the optimum acidity ranges were found to be in the range 0—6.0 mol/dm<sup>3</sup>.

### *Effect of Reagent*

A 4 and 250 fold molar excess of HCPCMPA and phenols were necessary for quantitative extraction of vanadium(V). Addition of more reagents (100 and 2000 fold molar excess of HCPCMPA and phenols respectively) had no adverse effect on the absorbance and  $\lambda$  max of the coloured complex. Order of addition of reagents was not critical.

### *Effect of Salting out Agents*

Lithium, sodium, potassium and ammonium chlorides were tested as salting out agents in the concentration range 0.5—3.0 mol/dm<sup>3</sup>, but these had no significant effect on the extraction.

### *Period of Equilibration*

The period of equilibration varied from 1—30 min. Extraction was quantitative after 1 min. It is therefore recommended to shake the mixture for at least 2 min.

### *Effect of Temperature and Aqueous Volume*

Variation in temperature from 15—40 °C and volume of aqueous phase from 10—60 ml did not produce any measurable change in the absorbance of the chloroform extracts. All the chloroform extracts are stable for at least 30 h at 27±2 °C.

### *Beer's Law, Optimum Concentration Range and Precision*

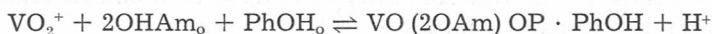
The vanadium concentration ranges, which adhere to Beer's law, and the optimum concentration ranges of vanadium as evaluated from steepest slope of the Ringbom plots are shown in Table I.

The precision of the systems was checked by measuring the absorbance values of 10 samples, each containing 100 µg vanadium/25 ml. The relative standard deviation of the methods lie within the range ±0.63—0.84%.

### *Nature of Extracted Species*

The ratio of vanadium to reagent in mixed complex was determined by mole ratio<sup>24</sup> and Job's method of continuous variations<sup>25</sup> and found to be 1 : 2 (metal : reagent). The ratio of vanadium to phenols was determined by the curve fitting method<sup>26</sup> (log absorbance vs log (mol/dm<sup>3</sup>) of phenols) in the presence of constant excess of reagent in chloroform and found to be 1 : 1 (metal : phenol). Thus the results obtained show the formation of 1 : 2 : 1 (metal : reagent : phenol) ternary complex in chloroform.

The extraction equilibrium of vanadiumHCPCMPA complex in the presence of phenols between chloroform and water may be expressed as



where o, HOAm, PhOH denote organic phase, hydroxyamidine and phenols respectively.

### Effect of Foreign Ions

For studying the effect of diverse ions on the determination, an aliquot of vanadium solution containing 100  $\mu\text{g}$  of the metal was transferred to a separatory funnel and a solution containing a known weight of diverse ions was added. The acidity was adjusted to 5.5 mol/dm<sup>3</sup> and the total volume to about 25 ml and vanadium was extracted with the reagent as described earlier. Chloride, bromide, sulphate, nitrate, phthalate, ammonia, tri-ethanolamine, urea, thio urea, alkali and alkaline-earth elements and lanthanoid elements had no interfering effect even if the weight ratio of these to vanadium was 1 : 600. The tolerance limits for other ions are given in Table II.

TABLE II

*Tolerance Limit for Diverse Ions on the Determination of Vanadium(V) Employing-HCPCMPA-p-Chlorophenol Ternary System at 5.5 mol/dm<sup>3</sup> Acetic Acid*

Ions added	Tolerance limit ppm in CHCl <sub>3</sub>	Ions added	Tolerance limit ppm in CHCl <sub>3</sub>
Fe <sup>3+</sup>	800	UO <sub>2</sub> <sup>2+</sup>	1200
Mo <sup>6+</sup>	350	Zn <sup>2+</sup>	2000
Ni <sup>2+</sup>	1800	Nb <sup>5+</sup>	150
Co <sup>2+</sup>	1800	Ta <sup>5+</sup>	150
Zr <sup>4+</sup>	75	Al <sup>3+</sup>	2000
Mn <sup>2+</sup>	1200	Tl <sup>3+</sup>	1200
Ti <sup>4+</sup>	100	Bi <sup>3+</sup>	1800
Cr <sup>3+</sup>	1000	Cu <sup>2+</sup>	250

### Application of the Method

The validity of the method was tested in two vanadium-tungsten steels, 64a (Alloy Steel) and 241/1 (High Speed Steel), and a tungsten free low alloy steel 252. The results are shown in Table III.

TABLE III

*Determination of Vanadium in Steels with HCPCMPA in Presence of p-Chlorophenol*

Steel	Certified value %	Vanadium found <sup>a</sup> %	S
64a Alloy Steel	1.57	1.558	±0.0068
241/1 High Speed Steel	1.57	1.554	±0.0085
252 Low Alloy Steel	0.46	0.450	±0.0073

BCS British Chemical Standard, Bureau of Analysed Samples, Ltd. Newham Hall Middlesbrough Yorks.

<sup>a</sup> an average of 6 determinations.

Dissolve a weighed quantity of sample containing about 3 mg of vanadium in 40 percent nitric acid. Tungsten was removed before the determination of vanadium as hydrated oxide by filtration with Whatman No. 42 filter paper. The vanadium content of the filtrate was determined as described in the previous procedure.

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## SAŽETAK

***N*-hidroksi-*N*-*p*-klorfenil-*N'*-(3-klor-4-metil)-fenil-*p*-toluamidin — novi osjetljiv i selektivan kromogeni reagens za ekstraktivno fotometrijsko određivanje vanadija(V) u nazočnosti fenola, *p*-klorfenola i 2-naftola**

*R. S. Kharsan i R. K. Mishra*

Predložena je nova metoda za ekstrakciju i spektrofotometrijsko određivanje vanadija(V), i to s pomoću *N*-hidroksi-*N*-*p*-klorfenil-*N'*-(3-klor-4-metil)-fenil-*p*-toluamidina (HCPCMPA) u nazočnosti fenolâ. Kompleksi HCPCMPA s vanadijem(V) očituju  $\lambda_{\text{max}}$  pri (595...625) nm, a molarni apsorpcijski koeficijent je u rasponu (6...7,6) · 10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. Mnogi ioni koji redovito dolaze zajedno s V, npr. Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, W<sup>6+</sup>, Mo<sup>6+</sup>, Mn<sup>2+</sup>, Nb<sup>5+</sup> i Ta<sup>5+</sup>, ne smetaju određivanju V predloženom metodom koja je povrh toga i primijenjena za određivanje V u standardnim uzorcima čelika.

SVEUČILIŠTE RAVISHANKAR  
RAIPUR-492 002  
INDIJA

Prispjelo 27. studenog 1978.