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N-Hydroxy-N,N′-diarylbenzamidine as a New Extraction System for Vanadium(V) in the Presence of Carboxylic Acids, Phenols, Aldehydes, Thiocyanate, and Azide*

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Abstract

N-Hydroxy-*N*-*m*-tolyl-*N*′-(2-methyl-5-chloro)phenyl-*p*-toluamidine hydrochloride (HTMCPTH) has been used as a new and convenient extraction system for vanadium(V) in the presence of all organic compounds containing -COOH, -CHO, -OH (phenolic) groups, and also in SCN^- and N_3^- media. HTMCPTH reacts with vanadium(V) to give a 1:2 complex (having a flat peak in the region 550–590 nm with 750 l/mole/cm). In the presence of various adduct-forming substances, a quantitative recovery of metal and marked absorbance enhancement into chloroform have been observed on the basis of formation and hyper- and bathochromic shift of the hydrophobic species formed. The extracting species is found to be 1:2:1 (V: HTMCPTH: RCOOH/ArCOOH/ArOH/ArCHO) and 1:2:2 (V: HTMCPTH: SCN^-/N_3^-) mixed complexes. The nature of adduct-forming substances has a large effect on absorbance and the λ_{max} of mixed complexes. The effective molar absorbances lie between 3500 to 8000 l/mole/cm. Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Mo^{6+}, etc. do not interfere. The method is accurately applied for determination of vanadium content in BCS steels.

INTRODUCTION

Recently, *N*-hydroxy-*N*,*N*′-diarylbenzamidines have been used as verasatile reagents for determining metal ions (*1–8*). A few hydroxyami-

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dines were first reported by Ley et al. (*9–10*) who studied their reducing properties but their analytical potential was recognized by Satyanarayana et al. (*1–3*). Hydroxyamidine offers several advantages over well-known reagents (*11–15*) in that by substitution of certain groups in the phenyl rings attached to the coordinating nitrogen, the complexing properties can be modified. Further, hydroxybenzamidine and its analogs gained wide popularity due to their very selective color reactions with vanadium (V) in the presence of various adduct-forming substances. Moreover, the reagents are stable to heat, light, and air, and their solution can be stored under proper conditions for a long time without deterioration.

Several monoprotic and bidentate chelating agents (*16–26*), which have been recommended as colorimetric reagents for vanadium(V), react with the metal to form 1 : 2 (metal : reagent) complexes which possess a basic VO group and an acidic VOH group in the same molecule. These complexes can react with various adduct-forming substances like carboxylic acids, phenols, mercaptans, alcohols, amines, hydrogen chloride, and other inorganic anions (*27–34*), giving rise to hyper- and bathochromic shift, and forming the basis for the spectrophotometric determination of vanadium(V).

The present work deals with the solvent extraction and subsequent spectrophotometric determination of vanadium(V) with *N*-hydroxy-*N*-*m*-tolyl-*N*′-(2-methyl-5-chloro) phenyl-*p*-toluamidine hydrochloride (HTMCPTH), a newly synthesized reagent, in the presence of various adduct-forming substances including carboxylic acids, phenols, aldehydes, thiocyanate, and azide. HTMCPTH reacts with vanadium(V) to develop a 1 : 2 (metal : ligand) complex. The basic VO group of this complex reacts with acidic substances including carboxylic acids and phenols to produce 1 : 1 adducts. It also reacts with vanadium(V) in the presence of thiocyanate and azide to give 1 : 2 : 2 (V : HTMCPTH : SCN^-/N_3^-) complexes accompanied by a hyper- and bathochromic shift. All these color reactions are capable of forming the basis for the development of sensitive and highly selective methods for the spectrophotometric determination of vanadium.

EXPERIMENTAL

A Carl Zeiss Specord recording ultraviolet and visible spectrophotometer and an ECIL GS-865 UV-VIS spectrophotometer equipped with 1-cm matched quartz and silica cells were used for measuring absorbance values. The pH values were determined with a Systronic pH meter, type 322.

All the chemicals and reagents used were of analytical reagent grade. A stock solution of ammonium metavanadate containing 0.50 g/l vanadium was prepared by dissolving B.D.H., AnalaR-grade substance in double distilled water and standardizing volumetrically (*35*).

The reagent was prepared by the condensation of equimolar amounts of *N*-(2-methyl-5-chloro) phenyl-*p*-toluimidoyl chloride with *N*-*m*-tolylhydroxylamine in ether medium (*36*). The resulting hydrochloride was recrystallized from absolute ethanol, mp 175°C, yield 65% (found: C = 66.10%, H = 5.46%, N = 6.80%; calculated for $C_{22}H_{22}N_{22}OCl_2$: C = 65.83%, H = 5.48%, N = 6.98%).

A 7.5×10^{-3} *M* solution of HTMCPTH in ethanol-free chloroform was used for extraction and spectrophotometric studies.

Procedure

Place an aliquot of vanadium(V) solution containing 100 μg of the metal in a 100-ml separatory funnel. Add a known quantity of the relevant adduct-forming substance either in aqueous or chloroform solution. Adjust the volume of the aqueous phase to 25 ml at the required pH. Extract the aqueous phase with a 10-ml chloroform solution of HTMCPTH for 2 min. Transfer the chloroform phase to a 50-ml beaker containing 2 g anhydrous sodium sulfate. Wash the aqueous phase with 2 × 4 ml portions of fresh chloroform. Transfer the combined extracts after drying into a 25-ml volumetric flask and dilute with chloroform to the mark. Measure the absorbance at the λ_{max} of the complex against chloroform as a blank.

RESULTS AND DISCUSSION

The wavelengths of maximum absorption and molar absorbances of the V(V)–HTMCPTH complex in the presence of various adduct-forming substances are summarized in Table 1. The absorption spectra of the V(V)–HTMCPTH complex and some of its adducts are shown in Figs. 1–4.

Choice of Solvents

All the vanadium adducts are extractable into such organic solvents as toluene, chloroform, carbon tetrachloride, benzene, and chlorobenzene. Such oxygenated solvents as higher alcohols and esters are unsuitable for extraction work because the ternary complexes are unstable and not

TABLE 1

Spectral Data for the Vanadium(V)–HTMCPTH Complex in the Presence of Various Adduct-Forming Substances in Chloroform (0.003 *M* HTMCPTH)

Adduct-forming substance	Concentration of adduct-forming substance (*M*)	Approximate pH range	Color[a]	λ_{max} (nm)	ε (l/mole/cm)	Sandell's sensitivity ($\mu g/cm^2$ V)
Formic acid	0.50[b]	0.2–25.0 *M*	BV	580	4800	0.0105
Acetic acid	1.00[b]	1.0–10.0 *M*	BV	575	4850	0.0105
Monochloroacetic acid	0.50[b]	0.1–10.0 *M*	BV	580	4900	0.0104
Acetoacetic acid	0.10[b]	0.8–5.0	BV	575	4700	0.0107
Phenylacetic acid	0.05[c]	1.0–6.0	BV	580	4800	0.0105
Diphenylacetic acid	0.05[c]	0.9–4.8	BV	580	5200	0.0098
Triphenylacetic acid	0.05[c]	0.8–5.0	BV	580	5300	0.0097
Naphthoxyacetic acid	0.05	1.0–5.2	B	590	6000	0.0084
Propionic acid	0.1[b]	1.0–4.5	BV	575	4450	0.0114
Butyric acid	0.10[b]	1.0–4.3	BV	575	4100	0.0124
Caprylic acid	0.10[c]	0.9–4.2	BV	570	4250	0.0119
Heptanoic acid	0.10[c]	1.0–4.2	BV	575	4250	0.0119
Undecylenic acid	0.10[c]	1.2–4.0	BV	565	4800	0.0106
Behenic acid	0.10[c]	1.2–3.8	BV	570	3650	0.0139
Benzoic acid	0.05[c]	1.0–4.5	BV	580	4450	0.0114
o-Chlorobenzoic acid	0.05[c]	0.8–4.5	BV	580	4950	0.0102
p-Chlorobenzoic acid	0.05[c]	0.9–4.5	BV	580	4900	0.0109
p-Toluic acid	0.05[c]	1.2–4.6	BV	575	3850	0.0132

Cinnamic acid	0.04[c]	1.0–4.6	BV	580	4600	0.0110
Anthranilic acid	0.04[c]	1.0–4.8	BV	570	4750	0.0107
N-Phenylanthranilic acid	0.03[c]	0.8–5.0	BV	580	5100	0.0099
Salicylic acid	0.03[c]	0.5–5.5	BV	585	5400	0.0094
Sulfosalicylic acid	0.03[c]	1.0–5.0	BV	585	5250	0.0097
Aspirin	0.03[c]	0.6–5.5	BV	580	5450	0.0093
Phthalic acid	0.03[c]	1.5–4.5	BV	580	5600	0.0090
Phenol	0.03[c]	0.9–3.2	B	600	6350	0.0080
p-Chlorophenol	0.03[c]	1.0–3.0	B	600	6700	0.0076
o-Cresol	0.03[c]	0.8–3.2	B	600	5000	0.0101
m-Cresol	0.03[c]	0.8–3.1	B	595	6050	0.0084
p-Cresol	0.03[c]	0.9–3.0	B	595	6050	0.0084
2-Naphthol	0.03[c]	1.0–3.0	GB	620	7300	0.0069
Benzaldehyde	0.06[c]	1.2–3.5	B	590	3500	0.0145
p-Hydroxybenzaldehyde	0.04[c]	0.8–4.5	B	590	8000	0.0064
Cinnamaldehyde	0.06[c]	1.0–4.0	B	590	3700	0.0137
Anisaldehyde	0.05[c]	1.0–4.5	GB	610	4600	0.0110
Vanillin	0.04[c]	0.8–5.5	GB	605	5100	0.0099
Thiocyanate	0.1[b]	0.8–3.5	DG	610	6000	0.0084
Azide	0.1[b]	0.4–2.5	B	590	5400	0.0094

[a] B = blue, BV = blue-violet, GB = greenish-blue, DG = dark green.

[b] Aqueous.

[c] Chloroform.

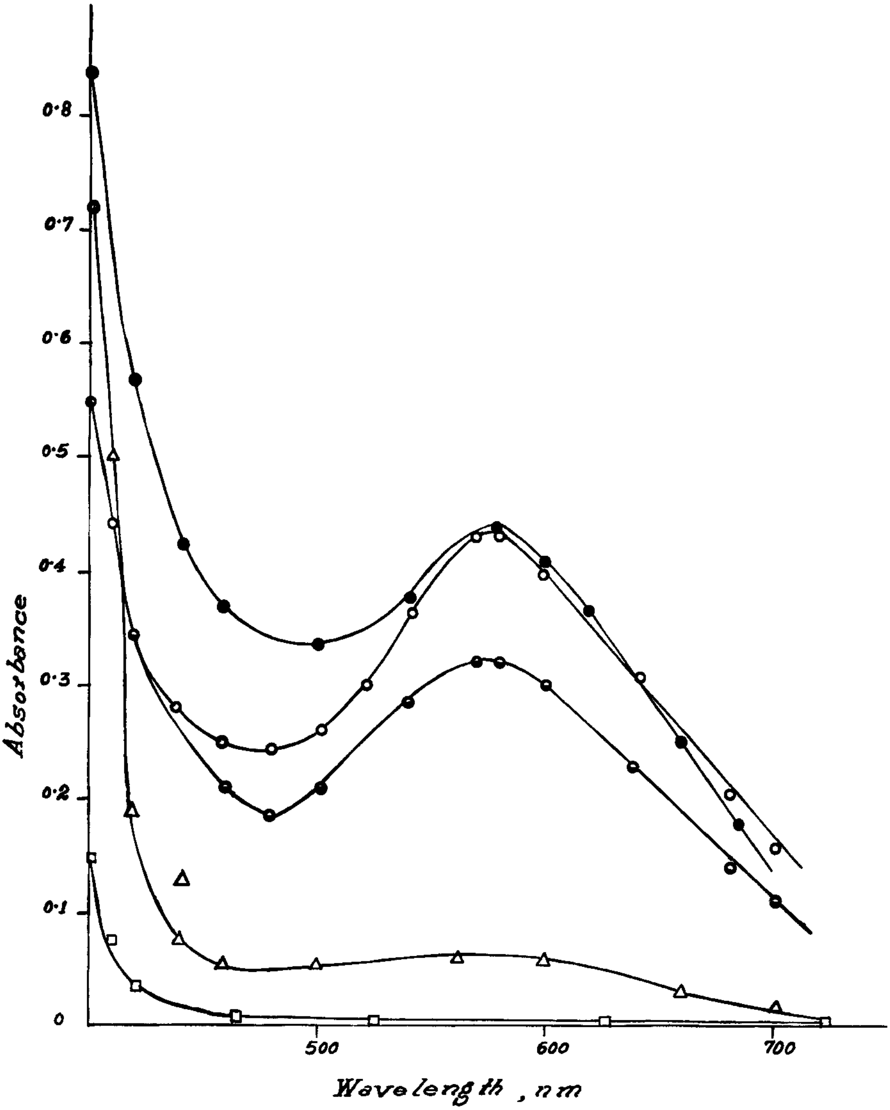

FIG. 1. Absorption spectra of reagent, vanadium(V) complex, and its carboxylic acid adducts. (●) Vanadium (8.00×10^{-5} M) + HTMCPTH (3×10^{-3} M) + aspirin (3×10^{-2} M). (○) Vanadium (9.66×10^{-5} M) + HTMCPTH (3×10^{-3} M) + benzoic acid (5×10^{-2} M). (◒) Vanadium (6.40×10^{-5} M) + HTMCPTH (3×10^{-3} M) + acetic acid (1 M). (△) Vanadium (7.85×10^{-5} M) + HTMCPTH (3×10^{-3} M). (□) HTMCPTH (3×10^{-3} M).

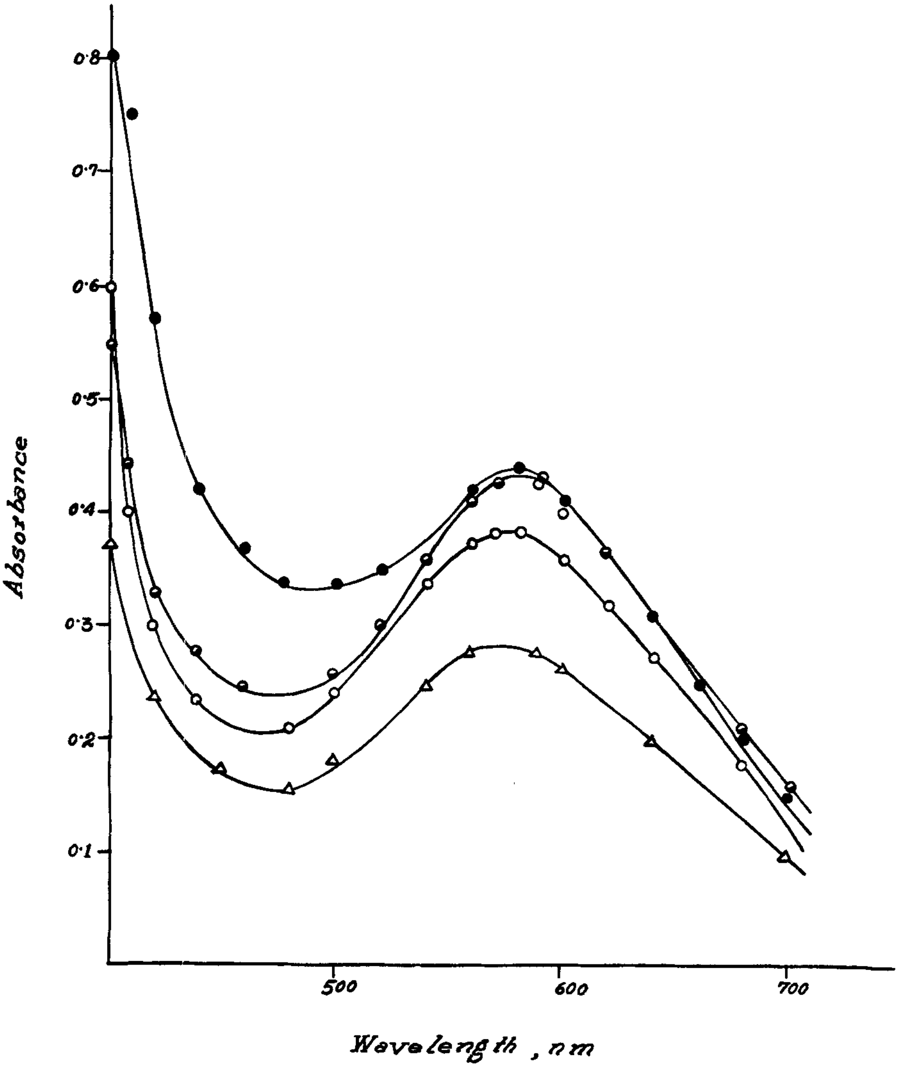

FIG. 2. Absorption spectra of carboxylic acid adducts. (●) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + phthalic acid (3 × 10^{-2} *M*). (◒) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + salicylic acid (3 × 10^{-2} *M*). (○) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + formic acid (5 × 10^{-1} *M*). (△) Vanadium (6.28 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + propionic acid (1 × 10^{-1} *M*).

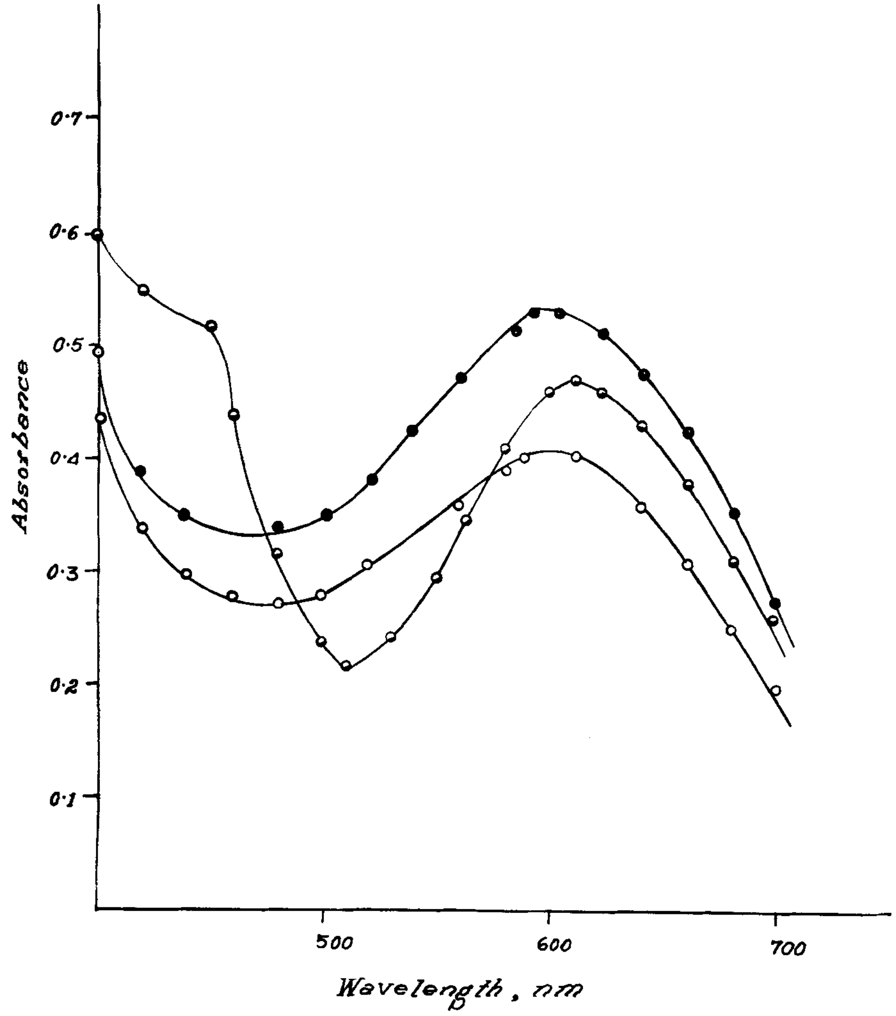

FIG. 3. Absorption spectra of phenol and thiocyanate adducts. (●) Vanadium (7.85×10^{-5} *M*) + HTMCPTH (3×10^{-3} *M*) + *p*-chlorophenol (3×10^{-2} *M*). (◒) Vanadium (7.85×10^{-5} *M*) + HTMCPTH (3×10^{-3} *M*) + thiocyanate (0.1 *M*). (○) Vanadium (6.28×10^{-5} *M*) + HTMCPTH ($3 \times$ $(10^{-3}$ *M*) + phenol (3×10^{-2} *M*).

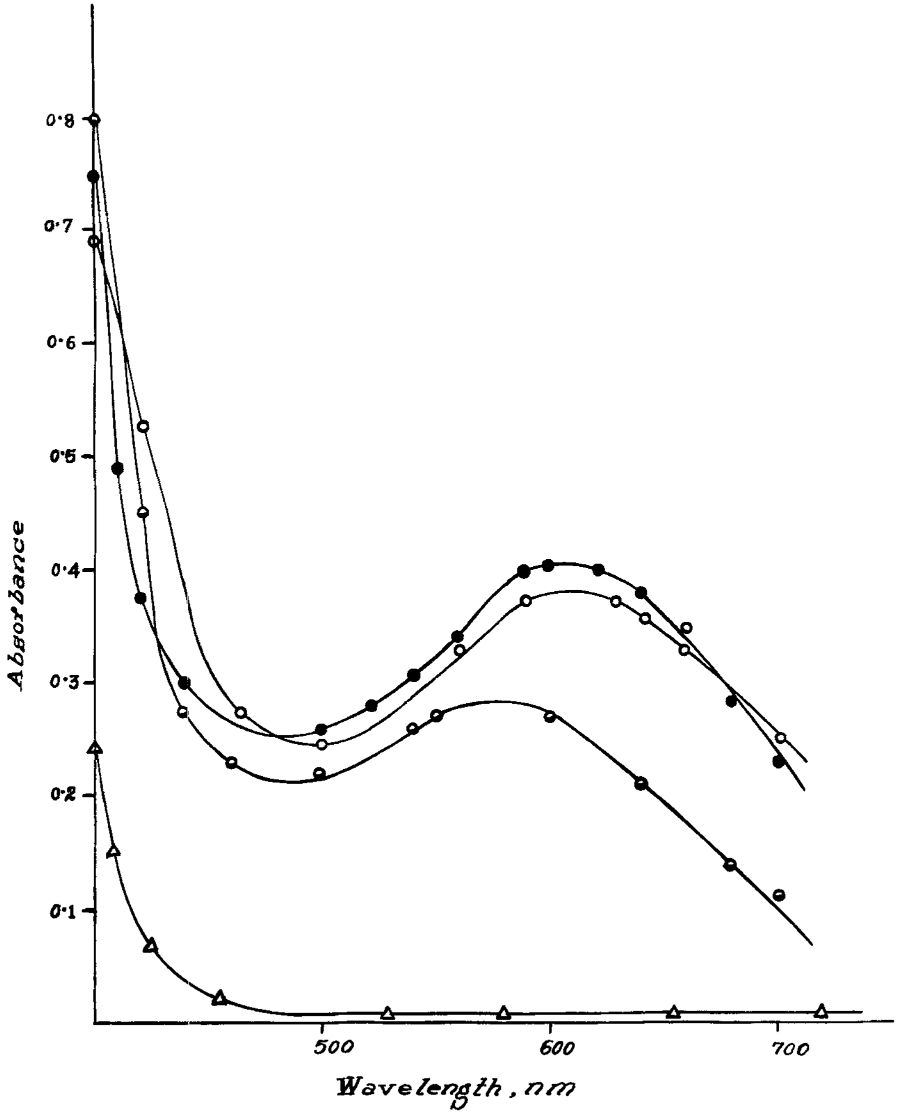

FIG. 4. Absorption spectra of aldehyde adducts. (●) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + vanillin (4 × 10^{-2} *M*). (○) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + anisaldehyde (5 × 10^{-2} *M*). (◒) Vanadium (7.85 × 10^{-5} *M*) + HTMCPTH (3 × 10^{-3} *M*) + benzaldehyde (6 × 10^{-2} *M*). (△) HTMCPTH (3 × 10^{-3} *M*).

sufficiently sensitive. Of these, chloroform was found to be the best reagent because vanadium complexes showed high distribution coefficients in it.

Effect of pH

The pH was maintained with 2 *M* hydrochloric acid and dilute ammonia. However, some strongly acidic substances such as acetic, monochloroacetic, and formic can provide wide acidity ranges for the extraction of vanadium(V), and they were used for acidity adjustment in their respective systems. The optimum pH ranges for different systems are summarized in Table 1.

Effect of Structure of Adduct-Forming Substances

The vanadium(V)–HTMCPTH complex forms 1 : 1 adducts with all the monobasic aliphatic carboxylic acids tested. Vanadium(V) is quantitatively extracted with carboxylic acids possessing up to 22 carbon atoms in the form of blue-violet adducts. The wavelengths of maximum absorption of V(V)–HTMCPTH–RCOOH complexes were in the range of 565–590 nm with molar absorbance values of 3650–6000 l/mole/cm. The optimum concentrations of carboxylic acids required for complete extraction of vanadium(V) are different for different kinds of acids used. The optimum concentration of HTMCPTH for complete extraction of vanadium(V) is related to the solubility of carboxylic acid in chloroform. The higher the solubility of carboxylic acid in chloroform, the lower is the necessary amount of HTMCPTH for complete extraction of vanadium(V). No adducts are formed with 1-hydroxy and dibasic carboxylic acids; e.g., oxalic, succinic, fumeric, malic, malonic, citric, tartaric, glycolic, and lactic. This may occur due to the complexation of vanadium(V) species with the above-mentioned acids. The addition of a phenyl group to the 1-carbon atom of the —COOH group may enhance the ease of adduct formation (e.g., mandelic acid forms an adduct with molar absorbance of 2050 l/mole/cm at λ_{max} 575 nm). In the acetic acid series the rate of extraction and the ease of adduct formation depend on the nature of the substituent in the CH_3COOH molecule. Aryl substituents enhance the molar absorbance and the rate of extraction to higher values, but electron-withdrawing substituents like halogen reduce the ease of adduct formation (no adducts are formed with $CHCl_2COOH$ and CCl_3COOH, which may be due to the high ionization constants of these acids). An increasing number of electron-releasing groups in the RCOOH molecule usually changes the absorbance to a lower value. This may be seen as due to the inductive (+1) effect of substituents in the —COOH group of the acid. The high +1 or −1 effect in the RCOOH molecule gives rise to low or even no synergistic effect, but high aromaticity enhances the ease of synergism to larger values. Thus it is confirmed that HCOOH, CH_3COOH, $CH_2ClCOOH$, and $Ar_nCH_{3-n}COOH$ (where Ar = phenyl/naphthyl, $n = 1, 2, 3$) are good adduct-forming substances in the RCOOH series.

Vanadium(V)–HTMCPTH complex forms 1:1 adducts with all monobasic, dibasic, 1-hydroxy, and 1-amino aromatic carboxylic acids and their derivatives in which the carboxylic group is retained in the molecule (e.g., aspirin, *N*-phenylanthranilic, sulfosalicylic). The wavelengths of maximum absorption of V(V)–HTMCPTH–ArCOOH adducts were in the range of 580–590 nm with molar absorbances between 3850 and 5600 l/mole/cm. A fourfold molar excess of HTMCPTH in chloroform is generally found to be sufficient for complete extraction of vanadium(V). Electron-withdrawing substituents such as —Cl, —OH, and —COOH also affect the molar absorbance and ease of adduct formation to higher values, but with electron-releasing substituents such as $—CH_3$ the reverse effect is observed. The extraction of vanadium(V) adducts into chloroform was faster with aromatic acids than with aliphatic ones.

The vanadium(V)–HTMCPTH complex forms 1:1 adducts with phenols in chloroform. A strong synergistic effect accompanied by hyper- and bathochromic shifts of the adducts formed in chloroform was observed. The absorption maxima of V(V)–HTMCPTH–ArOH adducts were in the region 595–620 nm with molar absorbances ranging between 5900 and 7300 l/mole/cm. Electron-withdrawing substituents such as —Cl enhance molar absorbance to larger values but the reverse effect is observed with electron-repelling substituents such as $—CH_3$. No adducts are formed with dihydric and trihydric phenols, which may be due to complexation of the vanadium(V) species. 2-Naphthol, which has the largest conjugation value, produces a vanadium(V) adduct which absorbs at a relatively longer wavelength and possesses the highest value of molar absorbance, 7300 l/mole/cm. At least a 3- and 250-fold molar excess of HTMCPTH and phenol, respectively, are adequate for complete extraction of vanadium(V).

The vanadium(V)-HTMCPTH complex forms 1:1 adducts with all aromatic aldehydes. The absorption maxima of aldehyde adducts were in the region 580–605 nm with values of molar absorbances of 3500 to 8000 l/mole/cm. A high synergistic effect is seen in the formation of the *p*-hydroxybenzaldehyde adduct compared to the benzaldehyde one. At least a 4- and

200 to 300-fold molar excess of HTMCPTH and aldehyde, respectively, were found to be necessary for complete extraction of vanadium(V). The aliphatic aldehydes were found to be unsuitable for extraction work.

HTMCPTH reacts with vanadium(V) in thiocyanate or azide media to produce a 1:2:2 (V:HTMCPTH:SCN^-/N_3^-) mixed complex extractable into chloroform. At least a sixfold molar excess of HTMCPTH and an 8- and 100-fold molar excess of thiocyanate and azide, respectively, are necessary for complete extraction of vanadium(V).

The ternary complexes of vanadium(V) are completely extracted within 1 to 5 min. The rate of extraction is found to be in the order $ArOH > SCN^- > N_3^- > ArCOOH > RCOOH > ArCHO$.

Volume of Aqueous Phase, Temperature, and Standing Time

The absorbance of colored systems was unaffected by variation of the volume of the aqueous phase between 15 and 60 ml. In practice, the volume of the aqueous phase was always adjusted to 25 ml before extraction. Variation in temperature of the aqueous phase from 20 to 35°C did not affect the absorbance values of the chloroform extract. The chloroform extracts were stable for at least 30 hr at 27 ± 2°C.

Effect of Electrolytes

The rates of extraction and absorbance of vanadium adducts are not affected by such electrolytes as ammonium acetate, ammonium chloride, potassium chloride, and sodium chloride (up to 3 *M*) because the distribution coefficients of the mixed complexes are high.

Beer's Law, Optimum Concentration Range, and Precision

The ternary systems follow Beer's law in the range of 0.5 to 12.5 ppm of vanadium(V). The optimum concentration, on the basis of the Ringbom plot (*37*), lies between 0.6 and 12.0 ppm of metal. The relative standard deviation of systems is found to be between ±0.5 and 1.0% (10 measurements were made, each containing 100 μgV/25 ml).

Effective Molar Absorptivities and Sensitivities

The effective molar absorptivities (calculated on the basis of vanadium content) of vanadium adducts lie in the range of 3500 to 8000 l/mole/cm.

The Sandell sensitivities (*38*) of color reactions are found to range between 0.0064 and 0.0145 μgV/cm^2.

Composition of Complexes

In V(V)–HTMCPTH–RCOOH/ArCOOH/ArCHO/ArOH complexes, the ratio of V to HTMCPTH was determined by Job's continuous method (*39*) and the mole ratio method (*40*). The ratio of V to the adduct-forming substance was evaluated by the curve fitting method (*41*) (by plotting the log absorbance vs log *M* of the adduct-forming substance). The results obtained indicate the formation of 1:2:1 (V:HTMCPTH:adduct-forming substance) complexes. In thiocyanate or azide systems the ratio of vanadium to HTMCPTH was determined by Job's method and the mole ratio method, and the ratio of V to SCN$^-$ or N$_3^-$ was determined by the slope ratio (*42*) and the mole ratio method. The results obtained suggest the formation of a 1:2:2 (V: HTMCPTH: SCN$^-$/N$_3^-$) ternary complex.

The overall reaction mechanism can be expressed as (*8*, *29*, *30*, *33*)

$$VO_2^+ + 2HOA_{m_o} + L_0 \rightleftarrows VO(OA_m)_2OH\cdot L_0 + H^+ \qquad (1)$$

$$VO_2^+ + 2HOA_{m_o} + 2X^- \rightleftarrows VO(X)_2OA_m\cdot HOA_{m_o} + OH \qquad (2)$$

where HOA_m = hydroxyamidine
L = RCOOH, ArCOOH, ArCHO, or ArOH
X^- = SCN$^-$ or N$_3^-$
o = organic phase

Effect of Diverse Ions

The influence of diverse ions on the determination of vanadium(V) was studied following the recommended procedures. Fe^{3+} reacts with HTMCPTH to give a violet color if the concentration of formic, acetic, or monochloroacetic acid of the aqueous phase is less than 4 *M*. It interferes seriously with the determination of vanadium(V). Interference due to Fe^{3+} can be eliminated by maintaining the acidity above 4 *M* formic, acetic, or monochloroacetic acid. However, Fe^{3+} interferes in other systems and was removed by masking it with trisodium phosphate (2 g). Mo^{6+} was found to react with HTMCPTH to form a chloroform-soluble light yellow extract in all systems, but it does not interfere with the determination of vanadium because the yellow color shows practically negligible absorption above 500 nm. Hence an excess of HTMCPTH was used in the presence of this metal under the condition employed. A small amount of W^{6+} can be tolerated in the determination. The oxidizing agents did not interfere in the present investigation.

Generally, large amounts of chloride, bromide, fluoride, iodide, nitrate, sulfate, phthalate, borate, iodate, persulfate, chlorate, phosphate, arsenate, urea, thiourea, triethanolamine, alkali and alkaline-earth elements, and lanthanoid elements do not interfere in all systems. The tolerated amounts of other ions (in ppm) which do not interfere with the determination of 4 ppm of vanadium are summarized in Table 2.

Application of the Methods

The validity of the present methods was tested by determining the vanadium content of standard steel samples obtained from the Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough, Yorks. The results are recorded in Table 3.

A weighed quantity (containing approximately 1 mg of vanadium) of the standard sample was placed in a 250-ml beaker and dissolved with

TABLE 2

Tolerated Amounts of Some Diverse Ions

	Amount tolerated (ppm)[a]				
Ion added	Formic acid	Phenol	Vanillin	Thiocyanate	Azide
Fe^{3+}	1200	800[b]	1000[b]	800[b]	900[b]
Cu^{2+}	800	300	200	350	400
Ni^{2+}	700	500	500	600	600
Co^{2+}	900	500	500	400	700
Zn^{2+}	1200	800	800	1000	1000
Cd^{2+}	1500	1000	1000	1200	1500
Mn^{2+}	800	500	500	600	800
Al^{3+}	1000	700	700	900	1000
Cr^{3+}	700	500	500	600	800
Ti^{4+}	60	100	120	200	300
Zr^{4+}	100	80	100	150	600
Nb^{5+}	100	100	120	80	150
Ta^{5+}	150	150	150	200	200
Mo^{6+}	300	200	200	100	200
W^{6+}	40	10	20	50	80
U^{6+}	600	500	500	500	600

[a] Error $<2\%$.

[b] In the presence of trisodium phosphate.

TABLE 3

Determination of Vanadium in BCS[a] Steels

No. and name of steel	System[b]	Vanadium found[c] (%)	Certified value (%)
64a alloy steel	A	1.560	1.57
	B	1.556	
	C	1.552	
	D	1.548	
	E	1.557	
241/1 high-speed steel	A	1.556	1.57
	B	1.553	
	C	1.546	
	D	1.552	
	E	1.555	
252 low alloy steel	A	0.450	0.46
	B	0.452	
	C	0.448	
	D	0.446	
	E	0.450	

[a] British Chemical Standards, Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough, Yorks.

[b] A = formic acid, B = phenol, C = vanillin, D = thiocyanate, E = azide.

[c] An average of six determination.

30% nitric acid. Tungsten was removed as hydrated tungstic oxide. The filtrate was evaporated to near dryness and finally transferred to a 100-ml volumetric flask and diluted to the mark. A 10-ml aliquot of the solution was pipetted into a 100-ml separatory funnel, and vanadium was determined according to the recommended procedures.

COMPARISION WITH OTHER METHODS

Several inorganic and organic reagents (*13*, *22*, *43–61*) have been recommended for the spectrophotometric determination of vanadium(V). All methods, except those employing tropolone and *N*-benzoyl-*N*-phenylhydroxylamine, lack selectivity and suffer from interference by Fe and one or more elements such as Cr, Cu, Ni, Co, and Mn which are commonly associated with vanadium in many alloys and complex materials.

N-Benzoyl-*N*-phenylhydroxylamine (*13*, *22*, *53*) has been commonly used as a selective reagent for the extractive photometric determination of vanadium(V) in hydrochloric acid media. Oxidizing agents, reducing agents, and Ti, Zr, and Mo interfere seriously. According to Shendrikar (*62*), Mn, Cr, Ti, Zr, Mo, and W interfere seriously in the determination of vanadium(V). It has been shown by some workers (*63*, *64*) that extraction is not quantitative because of the partial reduction of vanadium(V) in hydrochloric acid media. Donaldson (*23*) recently reported that this method yields low and erratic results.

A number of the drawbacks mentioned above are successfully eliminated in the proposed method. In the presence of various adduct-forming substances, no partial reduction of vanadium(V) is observed and hence the extractions are quantitative. Fe, Cr, Mn, Ti, Zr, and Mo do not interfere if formic, acetic, or monochloroacetic acid is employed. Another distinct advantage of the method is that vanadium can be determined in the presence of all organic compounds containing —COOH, —CHO, —OH (phenolic) groups and also in SCN^- and N_3^- media. Moreover, the complexing properties of the reagent can be modified by the introduction of substituents in the three phenyl rings attached to the coordinating nitrogen.

CONCLUSION

The proposed sensitive and highly selective methods are based on the extraction of vanadium(V) into chloroform as colored mixed chelates, with *N*-hydroxy-*N*-*m*-tolyl-*N*′-(2-methyl-5-chloro) phenyl-*p*-toluamidine hydrochloride and various adduct-forming substances including carboxylic acids, phenols, aldehydes, thiocyanate, and azide, and subsequent measurement of the absorbance of the extract. The present methods are relatively insensitive to such experimental variables as temperature, volume of aqueous phase, standing time, amount of reagents, and order of addition of reagents. The methods are accurate and precise. These methods do not involve the prior separation of iron associated with vanadium in alloy steels. Other elements such as Zn^{2+}, Cu^{2+}, Mn^{2+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, and Mo^{6+} do not interfere.

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