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Selective Extraction and Spectrophotometric Determination of Vanadium(V) with *N*-Hydroxy-*N*-*p*-chlorophenyl-*N*′-(2-methyl-5-chloro)phenyl-p-toluamidine Hydrochloride and Various Monobasic Carboxylic Acids

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Selective Extraction and Spectrophotometric Determination of Vanadium(V) with *N*-Hydroxy-*N*-*p*-chlorophenyl-*N*′-(2-methyl-5-chloro)phenyl-*p*-toluamidine Hydrochloride and Various Monobasic Carboxylic Acids

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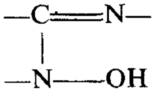
Abstract

N-Hydroxy-*N*-*p*-chlorophenyl-*N*′-(2-methyl-5-chloro)phenyl-*p*-toluamidine hydrochloride (HCPMCPTH), a newly synthesized bidentate chelating agent, reacts with vanadium(V) in the presence of monobasic carboxylic acids to give blue-violet water-insoluble adducts. The adducts have been extracted into various organic solvents such as chloroform, benzene, and carbon tetrachloride, and employed for the spectrophotometric determination of vanadium(V) and its separation from diverse ions. Investigations of the vanadium–HCPMCPTH–carboxylic acid complexes by spectrophotometric and solvent extraction techniques showed that the complex had the composition $VO(OAm)_2OH \cdot HOOCR$ (where HOAm = hydroxyamidine and HOOCR = carboxylic acid). The molar absorptivity and wavelength of maximum absorption of the mixed complex depend on the nature of the carboxylic acid used.

Vanadium(V) reacts with a number of monobasic and bidentate extracting agents containing —CO—C(OH)=, —CO—CH_2—CO—, —CO—N(OH)—, —N(NO)—O^-, =N—C(=)—C(OH)=, —C(OH)=C(—)—CH=N—OH, etc. groups to form colored complexes, usually having 1:2 metal to ligand stoichiometry (*1–5*). The complexes formed by these complexing agents probably contain a basic V=O group and an acidic V—OH group in the same molecule. Most likely the basic V=O group of the vanadium complex reacts with acidic substances such as carboxylic acids, hydrogen chloride, and phenols to give a hyper- and bathochromic effect.

N-Hydroxy-*N*-*p*-chlorophenyl-*N′*-(2-methyl-5-chloro)phenyl-*p*-toluamidine hydrochloride (HCPMCPTH), a newly synthesized reagent, possessing a new type of monobasic and bidentate functional grouping **1** (*6–11*) reacts with vanadium(V) in carboxylic acid media to give intensely colored complexes which are easily extracted into various organic solvents. This has been made the basis for the development of a highly selective method for the extractive separation of microgram amounts of vanadium(V) from a large number of diverse ions including molybdenum, titanium, iron, copper, chromium, cobalt, and manganese. The present paper deals with various aspects of extraction, separation, and simultaneous photometric determination of vanadium(V) using HCPMCPTH in carboxylic acid media. The method presented here is simple, rapid, and sensitive, and it can be applied to the determination of the vanadium content of complex materials. The present method has better selectivity than the established BPHA method (*12*).



$$\begin{array}{l}-\mathrm{C}{=}\mathrm{N}-\\ \quad|\\ -\mathrm{N}-\mathrm{OH}\end{array}$$

1

EXPERIMENTAL

A Carl Zeiss "Specord" ultraviolet-visible spectrophotometer and an ECIL UV-VIS spectrophotometer model GS-865 equipped with 1-cm matched quartz and silica cuvettes were used for recording the absorption spectra of the complexes and measuring the absorbance values, respectively. The pH values were determined by a Systronic pH meter type 322.

Analytical grade reagents were used throughout for preparing solutions of diverse ions. A stock solution of vanadium(V) (0.250 g/l) was prepared by dissolving ammonium metavanadate (0.5740 g/l) in double distilled water. The vanadium content of this solution was determined volumetrically using potassium permanganate (*13*).

HCPMCPTH was synthesized by the condensation of equimolar quantities of *N*-(2-methyl-5-chloro)phenyl-*p*-toluimidoyl chloride with

N-*p*-chlorophenylhydroxylamine in ether medium (*9*). The resulting hydrochloride was filtered and recrystallized from absolute ethanol, mp 164°, yield 73% (found: C = 59.70%, H = 4.35%, N = 6.26%; calculated for $C_{21}H_{19}N_2OCl_3$: C = 59.78%, H = 4.51%, N = 6.64%). A 1.0×10^{-2} *M* solution of the reagent in chloroform was used for extraction purposes.

Procedure

Place an aliquot of the solution containing 100 μg of vanadium(V) in a separatory funnel and add the desired quantity of the carboxylic acid. Dilute to 25 ml with water and extract with 10 ml of chloroform solution of HCPMCPTH. Dry the chloroform extract over anhydrous sodium sulfate and transfer to a 25-ml volumetric flask. Wash the aqueous layer with 2 × 5 ml portions of chloroform. Mix the dried washings in the same volumetric flask and dilute to mark with chloroform. Measure the absorbance at the wavelength of maximum absorption against chloroform as the blank.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of some carboxylic acid adducts of the vanadium(V)–HCPMCPTH complex are shown in Figs. 1A and B. When extracted in the absence of carboxylic acids, the vanadium–HCPMCPTH complex shows flat absorption maxima at 550–580 nm ($\varepsilon_{max} = 700$). However, in the presence of carboxylic acids a hyper- and bathochromic effect is observed. Thus the carboxylic acid adducts of vanadium–HCPMCPTH having their absorption maxima at 560–580 nm show ε in the range 3800–5400 l/mole cm. The wavelengths of maximum absorption along with the values of ε for each vanadium(V)–HCPMCPTH–carboxylic acid system are shown in Table 1.

Choice of Solvent for Extraction Work

Of the various organic solvents tested (benzene, toluene, xylene, chlorobenzene, *o*-dichlorobenzene, carbon tetrachloride, and chloroform), chloroform was found to be the most suitable for extracting the vanadium complex. This solvent was also preferred because of its low cost, easy

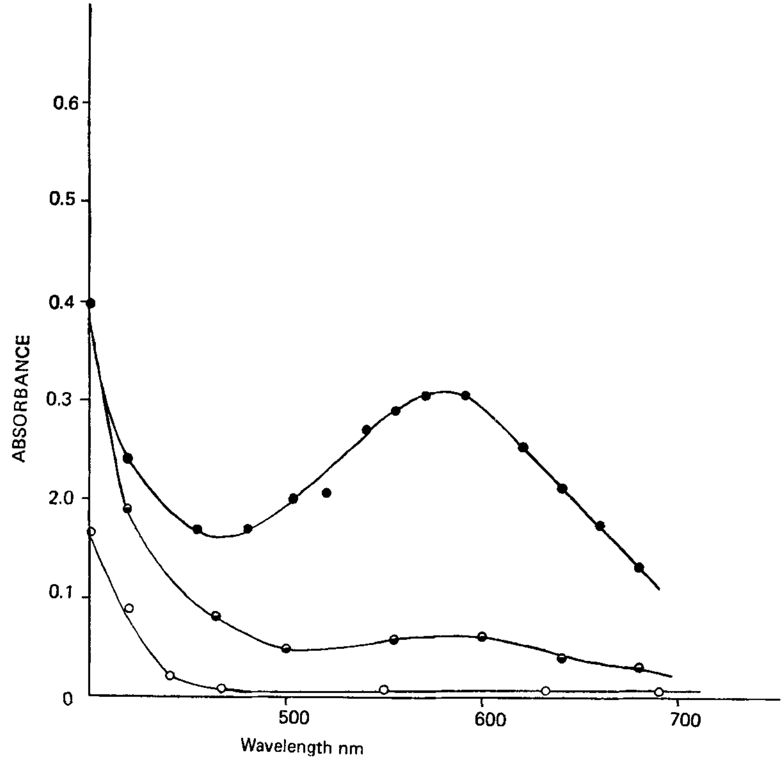


FIG. 1A. Absorption spectra. (●) Vanadium $(6.28 \times 10^{-5}\ M)$ + HCPMCPTH $(3.0 \times 10^{-3}\ M)$ + acetic acid (6*M*). (◒) Vanadium $(7.85 \times 10^{-5}\ M)$ + HCPMCPTH $(3.0 \times 10^{-3}\ M)$. (○) HCPMCPTH $(3.0 \times 10^{-3}\ M)$.

recovery, relatively higher solubility of HCPMCPTH in it than in other solvents, and its high extractability toward the adduct.

Effect of Acidity

Acetic acid was found to be best among the eighteen carboxylic acids employed for extracting the vanadium adduct because it may be used for extraction over a wide range of concentration (1 to 10.0 *M*). In the case of other carboxylic acids, the time required for complete extraction varies from 1 to 5 min whereas extraction is readily accomplished in acetic acid medium (1 min). Based on these facts, acetic acid was employed in subsequent studies for establishing the experimental variables. The optimum

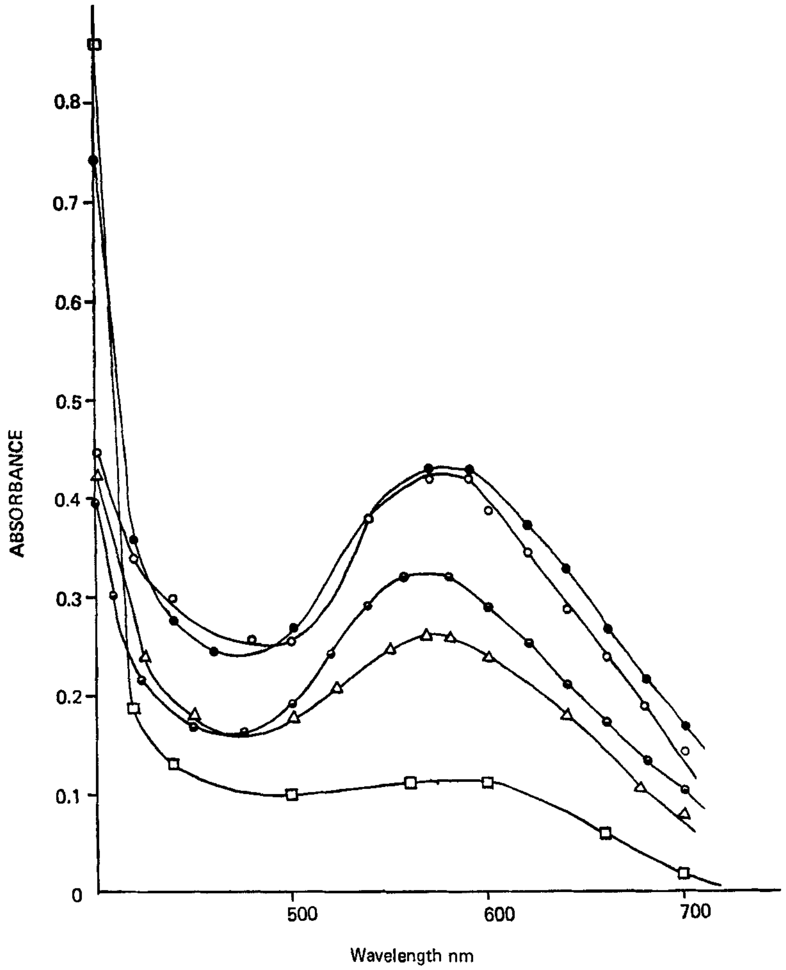


FIG. 1B. Absorption spectra. (●) Vanadium (7.85 × 10^{-5} *M*) + HCPMCPTH (3.0 × 10^{-3} *M*) + salicylic acid (3 × 10^{-2} *M*). (○) Vanadium (7.85 × 10^{-5} *M*) + HCPMCPTH (3.0 × 10^{-3} *M*) + formic acid (0.5 *M*). (◒) Vanadium (6.28 × 10^{-5} *M*) + HCPMCPTH (3.0 × 10^{-3} *M*) + *o*-chlorobenzoic acid (3 × 10^{-2} *M*). (△) Vanadium (6.28 × 10^{-5} *M*) + HCPMCPTH (3.0 × 10^{-3} *M*) + cinnamic acid (4 × 10^{-2} *M*). (□) Vanadium (1.57 × 10^{-4} *M*) + HCPMCPTH (3.0 × 10^{-3} *M*).

TABLE 1

The Wavelengths of Maximum Absorption and Molar Absorptivities of the Vanadium(V)-HCPMCPTH Complex in the Presence of Various Carboxylic Acids

Carboxylic acid	Concentration (M)	pH	λ_{max} (nm)	ε (l/mole cm)
	—	3.0	570	700
Formic	0.3[a]	2.5	580	5300
Acetic	1.0[a]	2.2	580	4700
Monochloroacetic	0.2[a]	2.6	580	5000
Butyric	0.2[a]	2.8	575	4400
Propionic	0.2[b]	2.9	570	4450
Heptanoic	0.1[b]	3.0	570	4000
Caprylic	0.1[b]	3.1	565	4300
Undecylenic	0.1[b]	3.0	560	4750
Benzoic	0.03[b]	3.1	575	4000
o-Chlorobenzoic	0.03[b]	2.9	570	4750
p-Chlorobenzoic	0.03[b]	3.0	575	5100
p-Toluic	0.03[b]	3.0	575	4050
Salicylic	0.03[b]	3.0	590	5200
Sulfosalicylic	0.03[b]	3.0	590	3800
Aspirin	0.02[b]	3.0	580	5400
Cinnamic	0.03[b]	3.2	575	4050
Anthranilic	0.03[b]	3.0	570	4050
N-Phenylanthranilic	0.03[b]	2.9	580	4850

[a] Aqueous phase.
[b] Organic phase.

molarity of acetic acid for extractions was 1.0 to 10.0 M. Above a molarity of 10.0 M acetic acid, low absorbance values were obtained.

Effect of HCPMCPTH Concentration

A 10-fold molar excess of the reagent was adequate for complete extraction of vanadium(V). The use of a 50:1 molar ratio of reagent to vanadium had no influence on the net absorbance of the vanadium complex.

Effect of Electrolyte, Temperature, and Time

Salting-out agents such as chlorides and nitrates of sodium, potassium, and calcium (1.0 to 3.5 M) have no significant effect on the extraction of vanadium(V) because the complex has a high distribution coefficient in chloroform. The intensity of the color attains a maximum at room temperature and is insensitive to variations of temperature of the aqueous phase in the 20 to 35°C range. The vanadium adduct is stable for at least 50 hr.

Beer's Law, Optimal Concentration Range, Sensitivity, and Precision

The vanadium adduct obeys Beer's law over the range from 1.0 to 9.5 ppm of vanadium(V). The optimum concentration range on the basis of Ringbom plot (*14*) is from 1.5 to 8.0 ppm of vanadium. The molar absorptivity of the blue-violet adduct in chloroform is 4700 l/mole cm, Sandell's sensitivity (*15*) being 0.011 μg of V/cm^2 at 580 nm. The relative standard deviation of the method has been found to be $\pm 0.60\%$ (calculated from the absorbance values of 10 samples, each containing 4 ppm of vanadium).

Composition of Ternary Complex

The ratio of vanadium(V) to HCPMCPTH was determined by Job's method (*16*) (Fig. 2) and the slope ratio (*17*) method, and that of vanadium(V) to acetic acid by the curve fitting method (*18*) (Fig. 3). The results obtained indicate the formation of a 1:2:1 (metal:HCPMCPTH:HOOCR) blue-violet adduct in chloroform solution.

Extraction Equilibrium of Vanadium–HCPMCPTH Complex in the Presence of Carboxylic Acids

The probable partition mechanism of the vanadium–HCPMCPTH complex in the presence of carboxylic acids between water and chloroform is expressed as follows (*1, 19, 20*). The overall reaction can be represented as

$$\mathrm{VO_2^+ + 2HOAm_o + HOOCR \rightleftarrows VO(OAm)_2OH\cdot HOOCR_o + H^+} \quad (1)$$

In the absence of carboxylic acids, a 1:2 metal: reagent complex is formed:

$$\mathrm{VO_2^+ + 2HOAm_o \rightleftarrows VO(OAm)_2OH_o + H^+} \quad (2)$$

In the presence of carboxylic acids, a 1:1 adduct is extracted:

$$\mathrm{VO(OAm)_2OH_o + HOOCR_o \rightleftarrows VO(OAm)_2OH\cdot HOOCR_o} \quad (3)$$

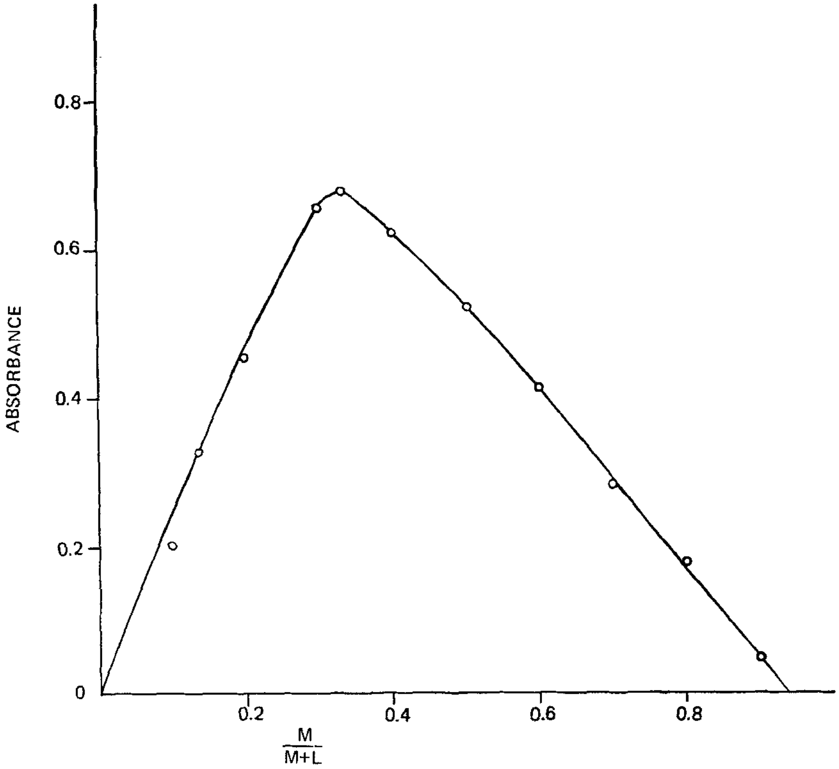


FIG. 2. Job's method of continuous variations. $C_V = C_{\mathrm{HCPMCPTH}} = 1.23 \times 10^{-3}\ M$; 5 M acetic acid.

The overall equilibrium constant β ($\beta = \beta_{1,2,0} \cdot \beta_{1,2,1}$) can be expressed as

$$\beta = \frac{[\mathrm{VO(OAm)_2OH}]_o[\mathrm{H^+}]}{[\mathrm{VO_2}^+][\mathrm{HOAm}]_o^2} \cdot \frac{[\mathrm{VO(OAm)_2OH \cdot HOOCR}]_o}{[\mathrm{VO(OAm)_2OH}]_o[\mathrm{HOOCR}]_o} \tag{4}$$

or

$$\beta = \frac{[\mathrm{VO(OAm)_2OH \cdot HOOCR}]_o[\mathrm{H^+}]}{[\mathrm{VO_2^+}][\mathrm{HOAm}]_o^2[\mathrm{HOOCR}]} \tag{5}$$

The distribution ratio $D_{1,2,1}$ is given by

$$D_{1,2,1} = \frac{[\mathrm{VO(OAm)_2OH}]_o[\mathrm{VO(OAm)_2OH \cdot HOOCR}]_o}{[\mathrm{VO_2^+}]} \tag{6}$$

$$= \beta_{1,2,0}[\mathrm{HOAm}]_o^2(1 + \beta_{1,2,1}[\mathrm{HOOCR}]_o)[\mathrm{H^+}]^{-1} \tag{7}$$

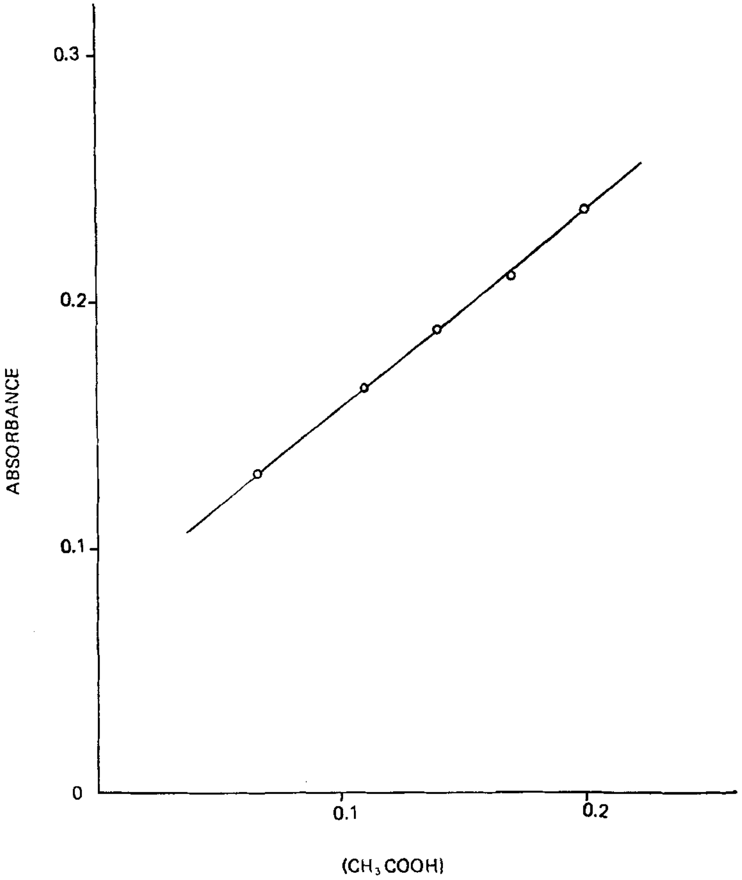


FIG. 3. Curve fitting method. Absorbance vs C_{HOOCCH_3}; $C_{HCPMCPTH} = 3.0 \times 10^{-3}$ *M*.

Subscript o, HOAm, and HCOOR denote organic phase, hydroxyamidine, and monobasic carboxylic acid, respectively.

Equation (1) depends on the nature of the carboxylic acid used. As the solubility of carboxylic acid in chloroform decreases, the optimum concentration of HCPMCPTH for complete extraction of vanadium(V) increases. In the acetic acid system a 10-fold molar excess of HCPMCPTH is adequate for complete extraction of the metal. In aromatic acid systems a 4-fold molar excess of HCPMCPTH is generally adequate for complete extraction of vanadium(V) into the organic phase. Similarly, Eq. (3) is applicable in the presence of 0.1 *M* $HOOC \cdot CH_2Cl$, 0.2 *M* $HOOC \cdot H$, 1 M HOOC·CH_3, and a 150 to 200-fold molar excess of aromatic carboxylic acids (in the presence of 0.003 M HCPMCPTH in chloroform).

Effects of Diverse Ions

To study the effects of diverse ions on the colored system, an aliquot of standard vanadium(V) solution containing 100 μg of vanadium was transferred to a separatory funnel and a solution containing a known weight of diverse ion was added. The acidity of the solution was adjusted to 5.0 to 6.0 M with acetic acid and the total volume to 25 ml. The blue-violet color was extracted from this solution in chloroform following the method described earlier. The tolerance limits for some foreign ions are listed in Table 2.

Fluoride, chloride, bromide, iodide, nitrate, sulfate, phosphate, borate, citrate, tartrate, selenate, arsenate, triethanolamine, urea, thiourea, alkali and alkaline earth elements, and lanthanides did not interfere with the determination of vanadium even when the weight ratio of any of the ions to vanadium was as high as 300 to 1. Tungsten (W^{VI}) inhibits color development.

Determination of Vanadium in Steels

Procedure

Dissolve a weighed quantity of steel containing 3.0 mg of vanadium in 40% nitric acid. Since tungsten interferes seriously, it must be removed

TABLE 2

Tolerance Limits of Some Diverse Ions (6 M Acetic Acid)

Ion added	Amount tolerated (ppm)	Ion added	Amount tolerated (ppm)
Fe^{3+}	800	Al^{3+}	500
Cu^{2+}	700	Cr^{3+}	500
Ni^{2+}	700	PO_4^{3-}	1000
Co^{2+}	700	AsO_4^{3-}	400
Zn^{2+}	1000	UO_2^{2+}	500
Cd^{2+}	1000	Mo^{6+}	300
Hg^{2+}	800	Ce^{4+}	400
Th^{4+}	800	Ti^{4+}	30
Tl^{3+}	1000	Zr^{4+}	50
Bi^{3+}	600	Ta^{5+}	100
Sb^{3+}	600	Nb^{5+}	100

TABLE 3

Determination of Vanadium in BCS[a] Steels

BCS Steel	Vanadium found[b] (%)	Certified value (%)
64a Alloy steel	1.54	1.57
241/1 High-speed steel	1.55	1.57
252 Low alloy steel	0.45	0.46

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

[b] An average of six determinations.

as hydrated tungstic oxide before estimation. Filter through a Whatman No. 42 filter paper and wash the beaker and the precipitate several times with hot water. Collect the filtrate in a 250-ml beaker, evaporate to near dryness, and dilute with water to a fixed volume. Determine vanadium from this solution as described earlier.

Two tungsten vanadium steels, 64a and 241/1, and a tungsten-free alloy steel, 252, were selected for the purpose. The results are shown in Table 3.

REFERENCES

1. I. Kojima and Y. Miwa, *Anal. Chim. Acta*, *83*, 329 (1976).
2. I. Kojima and M. Tanaka, *J. Inorg. Nucl. Chem.*, *29*, 1769 (1967).
3. O. Menis and C. S. P. Iyer, *Anal. Chim. Acta*, *55*, 89 (1971).
4. A. Blair, D. A. Pantony, and G. I. Minkoff, *J. Inorg. Nucl. Chem.*, *5*, 316 (1958).
5. I. Kojima and M. Tanaka, *Anal. Chim. Acta*, *75*, 367 (1975).
6. K. Satyanarayana and R. K. Mishra, *Anal. Chem.*, *46*, 1609 (1974).
7. K. Satyanarayana and R. K. Mishra, *Indian J. Chem.*, *13*, 295 (1975).
8. K. K. Deb and R. K. Mishra, *Curr. Sci.*, *45*, 134 (1976).
9. K. K. Deb and R. K. Mishra, *J. Indian Chem. Soc.*, *53*, 178 (1976).
10. K. K. Deb and R. K. Mishra, *Mikrochim. Acta*, Communicated.
11. K. K. Deb and R. K. Mishra, *Indian J. Chem.* In Press.
12. U. Priyadarshini and S. G. Tandon, *Anal. Chem.*, *33*, 435 (1961).
13. G. Charlot and D. Bezier, *Quantitative Inorganic Analysis*, Wiley, New York, 1957.
14. A. Ringbom, *Z. Anal. Chem.*, *115*, 332 (1939).
15. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959, p. 83.
16. P. Job, *Ann. Chim.*, *9*, 113 (1928).
17. A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, *72*, 4488 (1950).
18. L. G. Sillen, *Acta Chem. Scand.*, *10*, 185 (1956).
19. V. P. R. Rao and Y. Anjaneyulu, *J. Inorg. Nucl. Chem.*, *33*, 3567 (1971).
20. I. Kojima and M. Tanaka, *Anal. Chim. Acta*, *13*, 522 (1966).

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