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Analytical Study on Separation of Vanadium(V), Niobium(V), and Tantalum(V)

Sharad Mahadeo KAKADE and Vijay Malhar SHINDE*
Analytical Laboratory, Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Bombay 400032, India

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A simple and rapid method for extractive separation of vanadium(V), niobium(V), and tantalum(V) from halide media has been worked out using triphenylphosphine oxide in toluene as an extractant. The optimum conditions for extraction and separation have been evaluated from critical study of various variable factors. The log–log plots are used to ascertain probable extractable species. The method is applicable to the analysis of standard alloy samples and synthetic mixtures. The results are reproducible and accurate.

Both vanadium and niobium are industrially important elements. Vanadium foil is used as a bonding material between steel and titanium metal sheets. Vanadium imparts tensile strength, toughness, and elasticity to the steel. Niobium has potential value as electrolytic capacitors. Besides it promises to have an interesting future in the field of nuclear technology. In view of this, separation and purification of vanadium and niobium is desired.

Polar solvents such as diethyl ether,[1)] ethyl methyl ketone,[2—4)] tributyl phosphate (TBP),[5—7)] 3-hydroxy-2-methyl-4-pyranone,[8)] and mesityl oxide[9)] have been used for solvent extraction of vanadium, whereas diethyl ether,[10)] methyl isobutyl ketone (MIBK),[11)] and tributyl phosphate (TBP)[12)] have been used for extraction of niobium. The existing methods do not report mutual separation of vanadium(V), niobium(V), and tantalum(V); besides they suffer from limitations such as multiple extraction, co-extractions and use of high concentration of salting out agents.

In this paper, we propose a simple and rapid method for mutual separation of vanadium(V), niobium(V), and tantalum(V).

Experimental

Apparatus. Absorbance and pH measurements were taken on spectronic 20-D (milton Roy and Co.) and a Control Dynamics digital pH meter with combined glass electrode.

Reagents and Chemicals. The stock solution of vanadium(V) was prepared by dissolving 0.28 g of ammonium metavanadate in 3 $\mathrm{cm^3}$ of concentrated hydrochloric acid and diluted to 250 $\mathrm{cm^3}$ with distilled water. The solution was standardized titrimetrically.[13)] The stock solution of niobium(V) was prepared by fusing 0.071 g of diniobium pentaoxide (Koch-light) with 3 g of potassium disulfate. The obtained cooled melt was dissolved in 1 $\mathrm{mol\,dm^{-3}}$ tartaric acid and diluted to 100 $\mathrm{cm^3}$ with 1 $\mathrm{mol\,dm^{-3}}$ tartaric acid solution. For standard tantalum(V) solution, 2.5 g of ditantalum pentaoxide (Koch-light) was fused with potassium nitrate and potassium carbonate in the weight ratio 2 : 5 : 5. The cooled melt was dissolved in concentrated sulfuric acid. The acid was evaporated to almost dryness and the residue was dissolved in 20% tartaric acid and diluted to 100 $\mathrm{cm^3}$ with distilled water. Niobium and tantalum solutions were standardized with *N*-benzoyl-*N*-phenylhydroxylamine.[13)] The working solutions were prepared by suitable dilutions of stock solutions.

Fluka grade triphenylphosphine oxide (TPPO) dissolved in toluene was used for extraction studies. All other chemicals used were of analytical reagent grade.

General Extraction Procedure for Vanadium(V) and Niobium(V). Microgram amounts of vanadium(V) and niobium(V) are extracted from halide media with TPPO dissolved in toluene. The optimum extraction conditions are described in Table 1. After stripping, vanadium in aqueous phase is estimated spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR),[14)] whereas niobium(V) is estimated spectrophotometrically with thiocyanate in the organic phase itself.[13)]

Results and Discussion

Variation in hydrochloric and hydrobromic acid concentration (1—7 $\mathrm{mol\,dm^{-3}}$) and TPPO concentration (1—6.5%) using toluene as the diluent showed that the quantitative extraction of vanadium(V) occurs from 6—7 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid solution with 6.5% TPPO (Tables 2 and 3). Vanadium showed no extraction from hydrobromic acid solution. Niobium(V) however showed quantitative extraction from 5—6 $\mathrm{mol\,dm^{-3}}$ hydrochloric or 4.5 $\mathrm{mol\,dm^{-3}}$ hydrobromic acid with 6.0% TPPO. Tantalum(V) do not extract into TPPO either from hydrochloric or hydrobromic acid solution. The percentage extraction was evaluated by spectrophotometric determination.

The suitability of diluents was studied using solvents such as benzene, toluene, xylene, chloroform, and carbon tetrachloride. TPPO dissolved in toluene or benzene showed quantitative extraction of vanadium(V) and niobium(V). In other diluents extraction was incomplete.

Variation in shaking period showed that 60 s and 50 s equilibration was adequate for quantitative extraction of vanadium and niobium. Prolonged shaking forms emulsion and hinders phase separation.

Nature of Extracted Species. The nature of the extracted species was established with log–log plots. The log–log plot of distribution ratio versus TPPO concentration (at 6 $\mathrm{mol\,dm^{-3}}$ HCl for vanadium and 5 $\mathrm{mol\,dm^{-3}}$ HCl for niobium) gave a slope of 2.0 and 2.2 for vanadium and niobium respectively, indicating a molar ratio of 1 : 2 with respect to the extractant. Hence

Table 1. Optimum Extraction Conditions for Vanadium(V) and Niobium(V)

Metal ion	Aqueous phase	Organic	Shaking	Stripping	Estimation
μg	Total volume	phase	period	solution	process
Vanadium(V), 20	6—7 mol dm^{-3} HCl/10 cm^3	5 cm^3 of 6.5% TPPO in toluene	60 s	2×10 cm^3 of water	PAR[14]
Niobium(V) 10	5—6 mol dm^{-3} HCl/10 cm^3 or 4.5 mol dm^{-3} HBr/10 cm^3	5 cm^3 of 6.0% TPPO in toluene	50 s	—	Spectrophotometric estimation with thiocyanate in TPPO phase.[13]

Table 2. Extraction Behavior of 20 μg of Vanadium(V) as a Function of Acid Concentration and TPPO Concentration

Acid Concentration		TPPO concentration %	Percentage extraction
	mol dm^{-3}	%	of vanadium(V)
HCl	1.0	6.5	—
	2.0	6.5	26.5
	3.0	6.5	48.0
	4.0	6.5	73.5
	5.0	6.5	90.0
	6.0	6.5	99.5
	7.0	6.5	99.5
	6.0	1.0	—
	6.0	2.0	5.0
	6.0	3.0	40.0
	6.0	3.5	48.0
	6.0	4.0	56.0
	6.0	4.5	61.5
	6.0	5.0	67.0
	6.0	5.5	74.0
	6.0	6.0	77.5
	6.0	6.5	99.5
HBr	1—7	6.5	Nil

the extracted species is probably a solvated salt of the type $MOX_3 \cdot 2TPPO$, where M is either vanadium(V) or niobium(V), X stands for halide (either Cl^- or Br^-) and TPPO is triphenylphosphine oxide.

Effect of Foreign Ions. Varying amounts of foreign ions were added to a fixed amount of vanadium(V) (20 μg) and niobium(V) (10 μg) to study their interference. The tolerance limit was set at the amount required to cause ±1% error in the metal recovery. The results are reported in Table 4.

Separation of Vanadium(V), Niobium(V), and Tantalum(V). To an aqueous solution containing 10—20 μg each of vanadium(V), niobium(V), and tantalum(V), add hydrochloric acid so that its concentration is 6 mol dm^{-3} in a total volume of 10 cm^3, extract for 1 min with 5 cm^3 of 6.5% TPPO in toluene. Tantalum is not extracted and remains in aqueous phase. Evaporate the aqueous phase almost to dryness, add 5 cm^3 of water and determine tantalum with PAR against reagent blank.[13] Vanadium(V) from the organic phase is stripped with 2×10 cm^3 of water and determine spectrophotometrically with PAR against reagent blank.[14] Niobium(V) do not strip with water and remains in the organic phase; it is subsequently determined in the organic phase (TPPO) with thiocyanate at 430 nm.[13] The results of separation are reported in Table 5.

Analysis of Alloy. Electrical welding alloy containing niobium was analyzed by the proposed method. Since it does not contain vanadium, a known weight of vanadium was added and proposed procedure was followed for extraction, separation, and determination of vanadium and niobium.

A 50 mg of alloy was dissolved in 10 cm^3 of hydrofluoric acid, evaporated almost to dryness and residue was taken up in water. Filtered off the residue and filtrate was diluted to 100 cm^3. A 1 cm^3 aliquot containing 10 μg of vanadium and 15 μg of niobium was taken for extraction, separation and determination by the proposed procedure. The results of the analysis are reported in Table 6.

The method is very simple and permits rapid separa-

Table 3. Extraction Behavior of 10 μg of Niobium(V) as a Function of Acid Concentration and TPPO Concentration

Acid Concentration		TPPO concentration %	Percentage extraction
mol dm^{-3}		%	of niobium(V)
HCl	1.0	6.0	10.0
	2.0	6.0	20.0
	3.0	6.0	45.5
	4.0	6.0	75.2
	5.0	6.0	99.2
	6.0	6.0	99.2
	7.0	6.0	98.5
	5.0	1.0	—
	5.0	2.0	18.0
	5.0	3.0	49.0
	5.0	3.5	59.5
	5.0	4.0	67.0
	5.0	4.5	72.5
	5.0	5.0	78.0
	5.0	5.5	88.0
	5.0	6.0	99.5
	5.0	6.5	99.5
HBr	1.0	6.0	—
	2.0	6.0	18.0
	3.0	6.0	55.0
	4.0	6.0	82.5
	4.5	6.0	99.5
	5.0	6.0	98.2
	6.0	6.0	97.2
	7.0	6.0	97.4

Table 4. Effect of Diverse Ions on the Extraction of 20 μg of Vanadium(V) from 6 mol dm^{-3} HCl with 6.5 % TPPO in Toluene and 10 μg of Niobium(V) from 5 mol dm^{-3} HCl with 6.0% TPPO in Toluene

Ions	Tolerance limit/μg		Ions	Tolerance limit/μg	
	Vanadium(V)	Niobium(V)		Vanadium(V)	Niobium(V)
Ba(II)	5000	4500	Mo(VI)	None	50
Bi(III)	2000	2000	Hg(II)	500	400
Mg(II)	6000	2000	Zn(II)	4000	4500
Th(IV)	3000	2500	Sn(II)	1000	800
Pt(IV)	4000	3000	Ag(I)	2000	1500
In(III)	500	200	Au(III)	200	200
Tl(III)	300	100	Cr(VI)	100	200
Ga(III)	None	None	Ru(III)	2000	2000
Zr(IV)	4000	3000	Fe(III)[a]	40	50
Se(IV)	500	200	Be(II)	1500	1000
Os(III)	2000	1800	Citrate	5000	4000
W(VI)	1000	500	Tartrate	8000	7000
Cd(II)	1500	2000	EDTA	5000	4500
Al(III)	5000	4000	Oxalate	4000	3000
Ni(II)	4000	3000	Phosphate	3000	3000
Cu(II)	2000	2500	Thiourea	1000	500
Pd(II)	600	500	Thiosulfate	1500	2000
Ta(V)	500	600	Fluoride	1500	2000

a) Iron (III)-Masked with EDTA (1 mg).

tion and determination of microgram amounts of vanadium, niobium and tantalum. The average recoveries of these metals were ⩾99%. Each determination took 20—25 min.

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Table 5. Analysis of Synthetic Mixtures

Analysis No.	Mixture	Recovery[a]	Standard deviation	Coefficient of variation/%
	μg	%		
1.	V, 20; Nb, 10; Ta, 20	V, 99.6; Nb, 99.4; Ta, 99.2	V, 0.75×10^{-3}; Nb, 0.63×10^{-3}; Ta, 0.57×10^{-3}	V, 0.25; Nb, 0.36; Ta, 0.20
2.	V, 10; Nb, 20; Ta, 10	V, 99.3; Nb, 99.7; Ta, 99.6	V, 0.54×10^{-3}; Nb, 0.6×10^{-3}; Ta, 0.89×10^{-3}	V, 0.18; Nb, 0.18; Ta, 0.16
3.	V, 10; Nb, 10; Ta, 20	V, 99.9; Nb, 99.1; Ta, 99.2	V, 1.0×10^{-3}; Nb, 0.41×10^{-3}; Ta, 0.57×10^{-3}	V, 0.33; Nb, 0.11; Ta, 0.20

a) Average of six determinations.

Table 6. Analysis of Alloys

Alloy	Composition	Recovery of vanadium[a]/%	Recovery of niobium[a]/%
	%		
Electrical welding alloy	C, 0.67; S, 0.008; P, 0.02; Si, 0.9; Nb, 3.0; Pb, 0.029; Bi, 0.05; Ti, 0.05+1 mg V	99.0	99.3

a) Average of six determinations.

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