

TABLE 1 — EFFECT OF DIVERSE IONS ON THE EXTRACTION OF Pd(II) BY VARIOUS AMINES

[Pd(II) taken, 12.6 mg]

Foreign ions	Amount added (mg)	Pd extracted (%)			
		Triethyl-amine	Pyridine	2-Methyl pyridine	2,4,6-Tri-methyl pyridine
Ni(II)	80	97.5	99	98	98
Co(II)	80	98	98	97	96
Fe(III)	85	97	99*	98*	97*
Pt(IV)	40	97	97	97	98
Rh(III)	60	97	99	98	97
Ru(III)	40	96	98	97	97
U(VI)	95	97	98	99*	98*
Mn(II)	75	97	99*	98	99*
Zr(IV)	80	98	98*	97*	98*
Cd(II)	60	70	ppt	96*	97*
Hg(II)	80	96	ppt	98	98*
Cu(II)	65	97	98*	97*	97
Zn(II)	65	96	98	98	97*
Th(IV)	70	ppt	—	ppt	—
Al(III)	75	97	98*	98*	98*
Ca(II)	80	97	99	97	98
Ba(II)	80	97	98	97	98*
Sr(II)	80	96	97	97	96
V(V)	55	97	97	98*	97
EDTA	100	97	98	88	53
Tart ³⁻	100	98	97	97	97
Phosphate ³⁻	100	97	97	96	97
Borate ³⁻	100	96	97	98	98
Fluoride ⁻	100	98	98	99	98

*Extraction in the presence of ammonium hydrogen fluoride.

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**Determination of V(II) & V(III) with
Potassium Bromate, Potassium Dichromate,
Sodium Vanadate & Ferric Ammonium
Sulphate Using Cacotheline as Redox Indicator**

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The efficacy of cacotheline as an indicator in the estimation of V(II) and V(III) by conventional reagents is described.

USE of redox indicator, cacotheline, in the estimation of V(II) and V(III) by titration with well-known reagents like potassium bromate¹, ferric ammonium sulphate²⁻⁴, potassium dichromate^{5,6} and sodium vanadate^{6,7} is described.

The present method for the determination of V(II) using bromate is direct and less time-consuming¹. In other methods²⁻⁴, V(II) is oxidized to V(IV) by Fe(III) either at about 80° or in the presence of Cu(II) as catalyst. Ellis and Vogel⁸ reported that oxidation of vanadium(III) by iron(III) is slow at room temperature. In Rao and Murthy's method⁷ also, the estimation of V(III) was carried out at 45-50°C. However, in the present method V(III) can be titrated against Fe(III) at room temperature in acetic acid medium with normal speed.

Determination of V(II) using ferric ammonium sulphate—To the acetic acid (10M, 40 ml) was added Fe(III) solution (0.1N, 5 ml), carbon dioxide passed through it for 10 min and the titration carried out against V(II) solution adding 0.5 ml of cacotheline solution (0.2%) near the end-point. At the end-point a sharp change from yellow to pink colour was observed. It was found that a little amount of indicator was destroyed if added at the beginning, so the addition of the indicator near the end-point was recommended. Some typical results are presented in Table 1.

Determination of V(II) using potassium bromate—To 40 ml of hydrochloric acid (1M) was added 5 ml (0.1N) of potassium bromate, carbon dioxide passed through the contents for 10 min and the titration carried out against V(II) solution adding 0.5 ml cacotheline solution (0.2%) just before the end-point (pink colour). The results are given in Table 1.

Determination of V(III) using potassium dichromate, sodium vanadate or ferric ammonium sulphate—The required volume of gl. acetic acid and 5 ml

TABLE 1 — DETERMINATION OF V(II) AND V(III) USING VARIOUS OXIDANTS

Oxidant	Vanadium (mg)		Error (%)
	Taken	Found	
VANADIUM(II)			
Fe(III)	5.799	5.781	-0.31
	14.52	14.56	+0.27
	26.15	26.10	-0.19
Bromate	1.229	1.232	+0.24
	10.82	10.80	-0.19
	22.72	22.76	+0.18
VANADIUM(III)			
Fe(III)	3.221	3.227	+0.19
	16.39	16.42	+0.18
	31.49	31.42	-0.22
V(V)	2.875	2.869	-0.21
	10.71	10.72	+0.09
	16.12	16.10	-0.12
Cr(VI)	2.975	2.972	-0.10
	8.965	8.974	+0.10
	14.85	14.87	+0.14
	27.16	27.13	-0.11

of 0.1*N* oxidant solution were taken in a titration vessel and the contents diluted to 40 ml to produce the acetic acid concentration of 2*M* (in the case of vanadate), 4*M* (in the case of dichromate) or 6*M* [in the case of Fe(III)]. Carbon dioxide was passed through the contents for 10 min, and the titration carried out against V(III) solution adding 0.5 ml of cacotheline solution (0.2%) near the end-point (pink colour). The results are given in Table 1.

The indicator correction in all the above cases was 0.03 ml of 0.1*M* reductant solution.

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Extractive Spectrophotometric Determination of Ce(IV) with *p*-Anisidine

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A new extractive spectrophotometric method for the determination of Ce(IV) with *p*-anisidine is proposed. The reddish-violet complex can be quantitatively extracted at *pH* 2 (KCl-HCl buffer) by isoamyl alcohol in which solution it shows maximum absorbance at 510 nm. The complex has a molar composition of 1:1 and obeys Beer's law up to 20 ppm of Ce(IV).

SUTEU¹ has reported that *p*-anisidine forms a violet complex with V(V) in the presence of HCl (2.21*M*). We have observed that Ce(IV) also forms a violet complex at *pH* 2 with this reagent. The complex is stable in aqueous solution for 1 hr but if extracted in organic solvents it is stable for a longer time. This property has been utilized to

develop an extractive spectrophotometric method for the determination of Ce(IV).

The system attains maximum absorbance (λ_{\max} 510 nm) between *pH* 2 and 2.5 beyond which the λ_{\max} is changed. Subsequent experiments were done at *pH* 2. Amongst the buffers tried KCl-HCl buffer gave better results. The extraction of the complex was tried in various organic solvents. It was found that the complex is extractable in chloroform, isoamyl alcohol, amyl acetate and isobutyl alcohol. The choice of the solvent was made by finding the distribution coefficient and percentage extraction in each solvent. It was found that percentage extraction and distribution coefficient are highest in the case of isoamyl alcohol.

The linearity between absorbance and metal ion concentration was observed up to 20 ppm of Ce(IV). The sensitivity of the colour reaction as calculated from Beer's law plot was found to be 0.1 μg of Ce(IV)/ cm^2 for $\log I_0/I = 0.001$. The molar extinction coefficient for the complex is 1.68×10^3 .

Job's method of continuous variation was applied to find out the composition of the complex. The complex has 1:1 stoichiometry. The suggested method though tedious is justified by the higher extinction coefficient and greater stability of the complex. This method can also be used for the separation of Ce(IV) from other lanthanides.

Procedure—Ce(IV) solution (500 ppm) was prepared by dissolving Ce(SO₄)₂ in distilled water after adding appropriate amount of H₂SO₄ and was standardized by the usual method. Commercial grade *p*-anisidine was purified by recrystallization from water and its 1% solution was prepared in ethanol.

To a solution containing up to 20 μg of Ce(IV), 5 ml of 1% *p*-anisidine was added. The *pH* of the solution was adjusted to 2 with KCl-HCl buffer and volume made up to 25 ml. The complex was extracted in 10 ml of isoamyl alcohol and absorbance measured at 510 nm after filtering it through anhydrous sodium sulphate and appropriate dilution. The amount of Ce(IV) was then deduced from the calibration curve drawn under identical conditions.

Effect of diverse ions—The effect of diverse ions was studied by adding to the Ce(IV) solution (0.25 ml of 500 ppm) various cations and anions 10 times in excess. It was found that Cu²⁺, Ni²⁺, Co²⁺, Mg²⁺, Cl⁻, Br⁻, NO₃⁻ do not interfere but MnO₄⁻, Cr₂O₇²⁻ and Fe³⁺ interfere and hence should be absent.

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