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The Radiochemistry of Vanadium

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CHEMISTRY

The Radiochemistry of Vanadium

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December 1960

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $0.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of vanadium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of vanadium which might be included in a revised version of the monograph.

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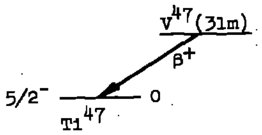
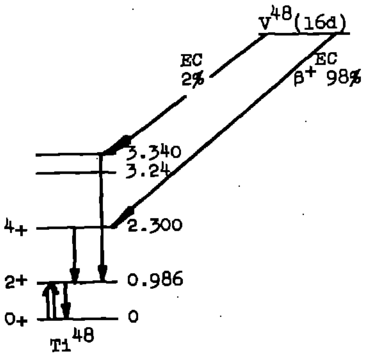
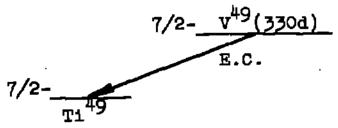
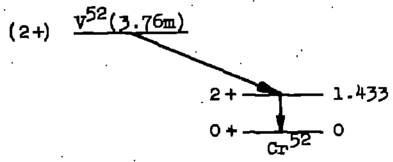
Note: References 2 through 5 contain general information on radiochemical separations, and are not specifically vanadium separation sources.

III. Table of Isotopes of Vanadium*

Isotope	Half Life (% Abundance)	Type of Decay	Method of Preparation	Decay Scheme (1)
$_{23}V^{46}$	0.4 sec.	$\beta^+ \geqslant 6.0$ Mev	$Ti^{46}(p,n)V^{46}$ (2) $Ti^{46}(d,2n)V^{46}$	
V^{47}	31 min.	β^+ 1.9 Mev	Cu(p,s)** (3) $Ti^{47}(d,2n)V^{47}$ $Ti^{46}(d,n)V^{47}$	
V^{48}	16 days	β^+ 0.69 Mev γ 0.986 1.314 2.25	$Ti^{48}(d,2n)V^{48}$ (4) Cu(p,s)** (3)	
V^{49}	330 days	E.C. 0.62	Cu(p,s)** (3) $Ti^{48}(d,n)V^{49}$ $Ti^{48}(p,\gamma)V^{49}$	
V^{50}	$4x10^{14}$ years (0.25%)	E.C.,	Naturally occurring	
V^{51}	(99.75%)	--	Naturally occurring	
$_{23}V^{52}$	3.76 min.	β^- 2.47 γ 1.43	$V^{51}(n,\gamma)V^{52}$ $Cr^{52}(n,p)V^{52}$ $Mn^{55}(n,\alpha)V^{52}$ $V^{51}(d,p)V^{52}$	
V^{53}	2 min.	β^- 2.50 γ 1.00	Cu(p,s)** (3)	
V^{54}	55 sec.	β^- 3.3 γ 0.835,0.99,2.21		

* References for much of the data contained in this table are found in Strominger, D., Hollander, J.M., Seaborg, G.T., Rev. Mod. Phys., 30, Pt. II, 585-904 (1958).

** The term s is used here to indicate spallation.

IV. REVIEW OF THOSE FEATURES OF VANADIUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. Metallic Vanadium

Pure metallic vanadium is extremely difficult to obtain, as it combines readily with carbon, nitrogen and oxygen, forming solid solutions with some of the products. Since vanadium is often produced by reduction of vanadium halides with dry hydrogen gas at elevated temperatures (5), hydrogen is often present in the metal, in addition to the above elements. The amounts of these contaminants may cause some interference or difficulty when their presence in an irradiated vanadium foil is not known.

Pure vanadium is fairly stable and is generally not subject to oxidation by moist air. In powdered form it burns in air to produce vanadium pentoxide; however, the reaction does not go to completion and some lower oxides are also formed. Volatile vanadium tetrachloride, VCl_4, is formed when vanadium metal is burned in an atmosphere of chlorine gas. This compound is also formed on heating vanadium with carbonyl chloride, surfuryl chloride, thionyl chloride or sulfur chloride at 600°C.

Vanadium metal is not readily attacked by aqueous solutions of alkali chlorides, bromine water, or cold hydrochloric acid, whether dilute or concentrated. The metal is attacked slowly by hydrofluoric acid and by hot, concentrated sulfuric acid. At 330°C, concentrated sulfuric acid reacts with metallic vanadium to produce vanadium pentoxide, V_2O_5, with evolution of SO_2; at lower temperatures, vanadium dioxide is formed, but is converted to the pentoxide on raising the temperature.

Metallic vanadium is readily attacked by cold dilute or concentrated nitric acid. Aqua regia also attacks the metal, vanadic acid being formed in either case. Vanadic acid is also formed by the action on vanadium of such oxidizing agents as chloric acid, perchloric acid, bromic acid, and potassium iodate. Soluble vanadates of sodium or potassium are produced when powdered vanadium metal is fused with sodium carbonate, potassium hydroxide or potassium nitrate.

2. Soluble Salts of Vanadium

Vanadic acid and vanadates of ammonium, lithium and the alkali metals are more or less soluble in aqueous solution. The vanadates are similar to the phosphates in that both anions are capable of condensing and forming poly-compounds. Starting with a highly alkaline solution of a vanadate and gradually reducing the pH, the following changes occur: in highly alkaline solution, the stable form is VO_4^{3-}; between pH 12 and 10, pyrovanadate, $V_2O_7^{4-}$, predominates. At about pH 9, $V_4O_{12}^{4-}$ is stable. These forms are all colorless. At pH values below 7, the solutions become highly colored, and vanadium pentoxide may precipitate. Below pH 2, the vanadium exists as pervanadyl ion, $V(OH)_4^+$, having a pale yellow color.

The chlorides, oxychlorides, fluorides, oxyfluorides, and bromides of vanadium are all fairly soluble in aqueous solutions. Many of these dissociate in aqueous solution to form complex ions.

Vanadium (IV) oxide combines with sulfuric, hydrochloric and hydrofluoric acids to form salts, which, when dissolved in water, give blue solutions.

Vanadium (III) is chemically similar to chromium (III) and iron (III), and forms aqueous soluble salts with most of the common acids. Soluble complexes are formed with fluoride, cyanide and ammonia.

Vandium (II) is similar to the divalent states of chromium and iron, and forms soluble salts with most acids, except those capable of undergoing reduction. Solutions of uncomplexed vanadium (II) are generally violet and are easily oxidized. Soluble complexes are formed with cyanide, fluoride, sulfate and ammonia.

Oxidation-Reduction Behavior

Pentavalent vanadium is reduced in acid solution by sulfite ion, or by bubbling SO_2 gas through an acid solution; vanadyl ion, VO^{2+}, is formed, having a blue color. Other methods for the reduction of vanadium (V) include: ferrous ion in acid; evaporation with hydrochloric acid, preferably in the presence of ferric iron and sulfuric acid (6); passage through a Jones reductor, in which vanadium is reduced to the bivalent state (7); reduction to the quadrivalent state by hydrogen sulfide (8), which is then expelled by boiling while CO_2 is blown through the solution; shaking with mercury in a dilute solution of hydrochloric or sulfuric acid (9) containing sufficient sodium chloride to precipitate the resulting mercury (I); reduction to the quadrivalent state by hydrogen peroxide in hot acid solution (10); and reduction to vanadium (IV) in a silver reductor.

Vanadium can be oxidized to the pentavalent state by nitric acid, but the reaction has been shown (11) to be only 99 per cent complete. Boiling perchloric acid, persulfate in the presence of silver ions, and hot excess permanganate in acid solution also oxidizes vanadium to vanadium (V).

In neutral solution, iodine, dichromate, and permanganate oxidize vanadium (II) to vanadium (III) if the addition is terminated at the phenosafranin change point. Iodine in a saturated solution of sodium carbonate oxidizes vanadium (IV) to vanadium (V). The text by Charlot and Bezier (12) gives several other procedures for the oxidation and reduction of vanadium compounds, as do many of the sources in section I.

3. Insoluble Salts of Vanadium - Precipitation and Co-precipitation Characteristics

A. Insoluble Salts

Some of the readily obtainable insoluble compounds of vanadium are listed in Table I. Many of the compounds listed offer possible means of separating radiovanadium from solution. The references listed in Parts I and II contain information on the use of certain of the compounds in separation and analytical procedures.

B. Co-precipitation Characteristics

Ammonium Phosphomolybdate as a Carrier for Vanadium

It has long been known that quinquevalent vanadium can be carried along with ammonium phosphomolybdate precipitates, imparting to these precipitates an orange or brick red color. That the precipitation can be made quantitative has been demonstrated by Cain and Hostetter (10,13), provided that the amount of phosphorous is five to ten times that of the vanadium. However, none of the vanadium is carried down if it is in the quadrivalent state and precipitation is made at room temperature (14). Coprecipitation of vanadium with phosphomolybdate affords a good means of separating vanadium from such elements as copper, chromium (VI), nickel, aluminum, iron, and uranium.

In order to make the separation, prepare the solution as for an ammonium phosphomolybdate precipitation, add ten times as much phosphorous as there is vanadium present, and then a slightly greater than usual excess of ammonium nitrate. Render nearly neutral by adding ammonium hydroxide, heat to boiling, add an excess of sodium molybdate solution, and shake for a few minutes.

Table I. Insoluble Compounds of Vanadium

Reagent(s)	Precipitate	Solubility	Remarks (Ref.)
Al^{+++}	$Al(VO_3)_3$ Aluminum metavanadate	Insoluble	Addition of Al^{+++} to neutral alkali vanadate; collodial white precipitate (17).
Ag^{+}	$Ag_3VO_4 \cdot xH_2O$ Silver orthovanadate	Soluble in HNO_3 and NH_4OH	Freshly prepared Na_3VO_4 treated with carefully neutralized $AgNO_3$; orange powder (5,17).
	$Ag_4V_2O_7 \cdot xH_2O$ Silver pyrovanadate	Insoluble as precipitated	Addition of neutral Ag^{+} salt to $Na_4V_2O_7$; yellow precipitate (5, 17, 18).
	$AgVO_3$ Silver metavanadate	$K_{sp} = 5x10^{-7}$	Addition of $AgNO_3$ to neutral NH_4VO_3; gelatinous yellow precipitate (5,17,18).
Ba^{++}	$Ba(VO_3)_2 \cdot H_2O$ Barium metavanadate	--	Precipitate at pH ~4.5 by adding $BaCl_2$ to NH_4VO_3 solution in acid. Stable up to 128°C. Loses H_2O 128-371°C to form stable anhydrous salt (5,17,18).
	$Ba_2V_2O_7$ Barium pyrovanadate	Insoluble as precipitated	Addition of $BaCl_2$ to solution of $Na_4V_2O_7$ in NH_4OH; white precipitate (5,17).
Bi^{+++}	$BiVO_4$ Bismuth orthovanadate	Insoluble as precipitated	Formed by double decomposition of alkali vanadate and $Bi(NO_3)_3$; bright yellow (7).
Ca^{++}	$Ca_2V_2O_7 \cdot xH_2O$ Calcium pyrovanadate	Insoluble as precipitated	Addition of $CaCl_2$ to $Na_4V_2O_7$ solution. $Ca_2V_2O_7 \cdot 5/2H_2O$ formed by drying at 100°C; white precipitate (17).
$Co(NH_3)_6^{+++}$	$[Co(NH_3)_6]_4(V_6O_{17})_3$	--	Precipitate in acetic acid at pH 5.1; gelatinous orange precipitate. Dry at 100-127°C. Ignites to $4CoO \cdot 9V_2O_5$ above 382°C (18).
	$[Co(NH_3)_6](VO_3)_3$	--	Precipitate under neutral or ammoniacal conditions. Dried between 58° and 143°C. Ignites to $2CoO \cdot 3V_2O_5$ between 600° and 950°C. Yellow-pink precipitate (18).
Cu^{++}	$Cu_3(VO_4)_2$ Cupric orthovanadate	Insoluble as precipitated	Precipitate by mixing Cu^{++} salts with soluble orthovanadates. Greenish-yellow precipitate (17, 18).
	$Cu_2V_2O_7 \cdot 3H_2O$ Cupric pyrovanadate	Insoluble as precipitated	Addition of $CuSO_4$ to solution of NH_4VO_3; greenish-yellow precipitate (17,18).
	$Cu(VO_3)_2$ Cupric metavanadate	Insoluble as precipitated	Colloidal precipitate formed by addition of Cu^{++} to neutral alkali vanadate. Green precipitate (17).
Fe^{+++}	$Fe(VO_3)_3$ Ferric metavanadate	Insoluble in H_2O and alcohol; acid soluble	Olive-green colloidal precipitate (17,19).
$Fe(CN)_6^{-4}$	$(VO)_2Fe(CN)_6$ Vanadylferrocyanide	--	Precipitation almost complete; V(V) gives no such precipitate. Greenish-yellow (15).
Hg_2^{++}	$Hg_2(VO_3)_2$ Mercurous metavanadate	--	Addition of $Hg_2(NO_3)_2$ to vanadate under nearly neutral conditions; loses weight between 60° and 670°C; V_2O_5 formed above 675°C. Orange precipitate (17,18,20).

Table I. Insoluble Compounds of Vanadium (Cont.)

Reagent(s)	Precipitate	Solubility	Remarks (Ref.)
Hg^{++}	$Hg(VO_3)_2$	--	Addition $HgCl_2$ to neutral vanadate solution; white precipitate (17).
$HPO_4^{=}+NH_4OH$	$VONH_4PO_4$ Vanadylammonium phosphate	--	(15).
H_2S+NH_4OH	V_2S_3 Vanadium trisulfide	Insoluble H_2O; soluble in alkali sulfides; slightly soluble in alkali, HNO_3, HCl and H_2SO_4	Thio-complexes probably formed in excess alkali sulfide. V(III) sensitive to air oxidation (19).
	V_2S_5 Vanadium pentasulfide	Insoluble H_2O; soluble in dilute HNO_3, alkali sulfides and alkalies	Thio-complexes formed in excess of sulfides (19).
In^{++}	$In(VO_3)_3 \cdot 2H_2O$ Indium metavanadate	--	Addition $InCl_3$ to $NaVO_3$; yellow precipitate (17).
Mn^{++}	$Mn(VO_3)_2 \cdot xH_2O$ Manganous metavanadate	--	Addition of $MnSO_4$ to NH_4VO_3; dark red, finely divided precipitate (17,18).
Ni^{++}	$Ni(VO_3)_2 \cdot xH_2O$ Nickel metavanadate	--	NH_4VO_3 solution boiled with slightly acidified $Ni(NO_3)_2$ in excess; greenish-yellow precipitate (17).
OH^-	$VO(OH)_2$	--	Brown precipitate.
Pb^{++}	$Pb_3(VO_4)_2 \cdot xH_2O$ Lead orthovanadate	Insoluble as precipitated	Lead acetate added to soluble orthovanadate; white powder (5, 17).
	$Pb_2V_2O_7 \cdot xH_2O$ Lead pyrovanadate	Insoluble at high temperature	Boil solution of $Pb(NO_3)_2$ and NH_4VO_3 in acetic acid (5,17).
	$Pb(VO_3)_2 \cdot xH_2O$ Lead metavanadate	Slightly soluble in H_2O; soluble in mineral acids	Acetic acid solution of vanadate plus lead salt (17,19,21).
Sn^{++++}	$Sn(VO_3)_4$ Stannic metavanadate	--	Large excess of Sn^{4+} required for precipitation; yellow precipitate (15).
Th^{++++}	$ThV_2O_7 \cdot 6H_2O$ Thorium pyrovanadate	Insoluble in H_2O; soluble in concentrated acids	(5,17,19).
Tl^+	$Tl_4V_2O_7$ Thallium pyrovanadate	$K_{sp}^{14^\circ} \sim 6x10^{-12}$ $K_{sp}^{100} \sim 2.6x10^{-11}$	Addition of Tl_2SO_4 to cold saturated solution of Na_3VO_4; light yellow precipitate (5,17, 22).
Tl^+	$TlVO_3 \cdot xH_2O$ Thallium metavanadate	$K_{sp}^{11^\circ} \sim 8.2x10^{-6}$ $K_{sp}^{100^\circ} \sim 4.8x10^{-5}$	Greenish-yellow precipitate (22).
UO_2^{++}	-- Ammonium uranyl orthovanadate	--	Dry at 105°C (18).

Filter the orange or brick red precipitate and wash with a hot solution of ammonium sulfate acidified with dilute sulfuric acid.

Titanium Hydroxide as a Carrier for Vanadium

That vanadium can be carried by the precipitation of titanium hydroxide can be shown in the following manner (15): a mixture of quadrivalent titanium and pentavalent vanadium in hydrofluoric acid is treated with concentrated ammonium hydroxide, forming a large white precipitate. To this precipitate is added a solution of ammonium sulfide, $(NH_4)_2S$, which turns the precipitate grayish-black. There is no evidence for the reddish color of thiovanadate either in the filtrate from the ammonium hydroxide precipitation, nor in the excess ammonium sulfide added to the precipitate of $TiO(OH)_2$ which carries the vanadium. When a solution of vanadate is added to the excess of ammonium sulfide, the characteristic red color of thiovanadate appears.

Vanadium may or may not be coprecipitated quantitatively by titanium hydroxide, depending upon the ratio of titanium to vanadium; 50 mg of vanadium is completely precipitated in 200 mg of titanium in the ammonium hydroxide precipitation. The method offers at least a partial, if not a complete, separation of vanadium from antimony, tin, tungsten, molybdenum, tellurium, copper, nickel, cadmium, and cobalt.

Other Co-precipitating Agents

The retention of vanadium by aluminum, ferric, and chromium hydroxides has been investigated (16). It has been noted that the retention corresponds to the adsorption process. Coprecipitation has been shown to take place for semi-micro and micro amounts of vanadium. The relative coprecipitation strengths on the hydroxides are $Al > Cr > Fe$.

4. Complex Ions of Vanadium

Vanadium forms many complex ions with organic and inorganic ligands. Several of these are of use in ion exchange and solvent extraction procedures. These methods, and their dependence to a large extent upon complex ions of vanadium, are discussed in later sections.

Several conplex ions involving vanadium are listed in Table II, which also lists conditions of complex formation and stability constants, where known. Vanadium forms several complexes other than those listed in Table II; these are separated into complexes involving the major valence states of vanadium and are discussed in the sections which follow.

A. Complexes of Pentavalent Vanadium:

Sulfate, oxalate and tartrate form complex ions with pentavalent vanadium in aqueous solution. These complexes are all of the "ato-" type, in which the oxygen of the ligand is coordinated to the VO^{3+} or VO_2^+ species.

The existence of oxalate complexes of pentavalent vanadium has been demonstrated clearly by Rosenheim (23). Vanadium solutions treated with alkali or ammonium oxalates form clear yellow solutions. The complex is sufficiently stable that no precipitate forms on addition of solutions containing calcium salts except in the presence of excess oxalate. In addition, vanadium is found only as the anionic species. Souchay (24) proposed that the complex be written $VO_2(C_2O_4)_2^{3-}$; and that the complex-forming reaction be given by

$$V_3O_9^{3-} + 6C_2O_4^{2-} + 6H^+ \longrightarrow 3VO_2(C_2O_4)_2^{6-} + 3H_2O$$

Souchay has also found (24) that in tartrate medium two complexes of vanadium are formed. In the presence of a large excess of tartrate in neutral solution, a 1:1 complex (structure I)

Table II. Complex Ions of Vanadium*

Complexing Agent	Reaction	Ionic Strength	T, °C	K	Ref.
OH^-	$V^{3+} + HOH \rightleftharpoons V(OH)^{2+} + H^+$	Varied	25	2×10^{-3}	a
		Varied	25	1.26×10^{-3}	b
	$V^{3+} + 2HOH \rightleftharpoons V(OH)_2^+ + 2H^+$	Varied	25	4×10^{-7}	b
	$VO^{2+} + HOH \rightleftharpoons VOOH^+ + H^+$	Varied	25	4.36×10^{-6}	b
		Corrected to 0	20	1.7×10^{-5}	c
		3	25	1×10^{-6}	d
	$2VO^{2+} + 2HOH \rightleftharpoons (VOOH)_2^{2+} + 2H^+$	3	25	1.32×10^{-7}	d
	$2VOOH^+ \rightleftharpoons (VOOH)_2^{2+}$	3	25	1.26×10^{5}	d
CN^-	$VO^{2+} + 2CN^- \rightleftharpoons VO(CN)_2(s)$	Varied	--	--	e
	$VO^{2+} + 6CN^- \rightleftharpoons VO(CN)_6^{4-}$	Varied	--	--	e
SCN^-	$V^{3+} + SCN^- \rightleftharpoons VSCN^{2+}$	2.6	25	1×10^{2}	f
	$VO^{2+} + SCN^- \rightleftharpoons VOSCN^+$	2.6	25	8.3	f
	$V^{3+} + 6SCN^- \overset{?}{\rightleftharpoons} V(SCN)_6^{3-}$	3.89f SCN^-	--	--	f
O_2^{2-}	$VO^{3+} + H_2O_2 \rightleftharpoons VO_3^+ + 2H^+$	Varied (H_2SO_4)	20	4.15×10^{3}	g
		Varied	--	3.3×10^{4}	h
		Dilute	18-20	1.29×10^{4}	i
	$VO_2^+ + H_2O_2 \rightleftharpoons VO_4^- + 2H^+$	20% H_2SO_4	20	8.1×10^{4}	j
	$\overset{?}{\rightarrow} H_2V_2O_4(O_2)_3^{2-}$	Varied	25	--	k,l
	$\overset{?}{\rightarrow} HV_2O_4(O_2)_3^{3-}$	Varied	25	--	k,l
	$\overset{?}{\rightarrow} V_2O_4(O_2)_3^{4-}$	Varied	25	--	k,l
F^-	$VO^{2+} + F^- \rightleftharpoons VOF^+$	Corrected to 0	25 (?)	1.41×10^{3}	m

* Data abstracted from "Stability Constants of Metal-Ion Complexes," Part II, Inorganic Ligands, compiled by Bjerrum, J., Schwarzenbach, G., and Sillen, L.G., The Chemical Society, London, 1958.

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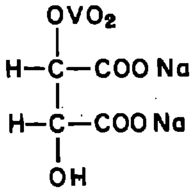
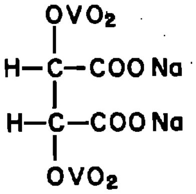
l. ibid, 47B, 705 (1951)
m. Ducret, L.P., loc. cit., 6, 769 (1951)

is formed. If a V:tartrate ratio greater that 1:1 is maintained, a complex is formed involving two vanadium and one tartrate ion (structure II).



Structure I



Structure II

Solutions of these complexes are garnet-colored. Addition of alkli causes conversion of the complex to tartrate and vanadate, while acidification below pH 5 converts the complexes to the acid salts of the complex tartrates.

A recent publication by Feigl (25) points out the masking effect of fluoride ions on some characteristic reactions of pentavalent vanadium. Reactions occurring in the presence and absence of fluoride ions are compared in Table III. In order to account for the anomalous behavior of pentavalent vanadium in the presence of fluoride ions, Feigl postulates the existence of a fluoro-complex of a type which allows for only a small equlibrium concentration of the simple vanadium species in solution. Feigl further postulates that the complex is of the type formed by replacing one of the oxygen atoms coordinated to the vanadium by two fluoride atoms.

Little information has been reported on the occurrence of pentavalent vanadium - chloride complexes; however, it is known that a brownish-yellow to brown complex is formed between pentavalent vanadium and chloride ion in strong hydrochloric acid solutions.

Table III

Masking Effect of Fluoride Ion on Vanadate

Without F^-	Reaction	With F^-
Blue color	Zn + HCl	No reaction
Yellow precipitate	$AgNO_3$	No reaction
Green precipitate	$K_4Fe(CN)_6$	Yellow precipitate
Yellow-red color	H_2O_2	No reaction
Green precipitate	Benzidene	Violet precipitate
Brown precipitate	8-hydroxyquinoline	Blue-green color
Red-brown precipitate	cupferron	Red-brown precipitate

B. Complexes of Tetravalent Vanadium

Tetravalent vanadium forms a large number of complexes, all of which involve the vanadyl group, VO^{2+}, and most of which are "ato-" complexes. Evidence has been found (26-28) for the vanadyl—thiocyanate complexes $VO(SCN)_4^{2-}$ and $VOSCN^+$ the latter complex appears not to be very stable. There is some evidence (28) for the occurrence of higher complexes in very concentrated thiocyanate solutions.

Two series of oxalato complexes have been reported by Koppel and Goldman (26). The complex most readily formed is of the form $H_2(VO)_2(C_2O_4)_3$.ag, which gives a positive test for oxalate in aqueous solution. A large excess of ammonium oxalate gives rise to the second series of oxalate complexes, represented by $M_2VO(C_2O_4)_2.2H_2O$. Sodium and potassium oxalates, even in high concentrations, do not form complexes of this type. No test for oxalate ion is obtained in aqueous solutions of the pure monovanadyl complex.

Sulfate and sulfite complexes have been observed (29), which are analogous to the oxalate complexes. The sulfite complexes are prepared by treating vanadate solutions with sulfur dioxide and alkali sulfites. The first sulfite complex has the composition $M_2O.3VO_2.2SO_2$. On adding excess sulfite, a clear green solution, corresponding to $VO(SO_3)_2^{2-}$, is formed.

Rivenq (30) reports the formation of cyanide complexes from $VO(CN)_6^{4-}$ through $VO(CN)_2$. Since a sixfold coordination about a central VO^{2+} ion would be required, the existence of the $VO(CN)_6^{4-}$ complex is questionable. No such coordination has been found for other ligands, and it is doubtful that it exists in the case of cyanide.

Ducret (31) has suggested the existence of weak fluoro complexes at a pH of approximately three. These appear to have little value in radiochemical separations. A tartrate and two citrate complexes are also formed with the vanadyl ion. The stability in alkaline medium of the two citrate complexes lies between that of the tartrate and the oxalate complexes, the oxalate being the less stable of the two.

Malonate, salicylate, catechol, and several other organic ligands form complexes of the ato-type with vanadyl ion. Several of these are insoluble in aqueous medium, and have been used for the gravimetric estimation of vanadyl vanadium.

C. Complexes of Trivalent Vanadium

Among the complexes of trivalent vanadium, which exists only as a metallic V^{3+} (hexahydrated) ion in aqueous solution, the halogens and halogenoids are formed most readily. Fluoride ions form the following complexes: VF_6^{3-}, $VF_5^{2-}. H_2O$, $VF_4^{-}. 2H_2O$ (32). Chloride ion forms the $VCl_5^{2-}. H_2O$ complex. The cyanide complex (33) has been isolated, but is unstable in aqueous solution. Several thiocyanate complexes have been reported (28,33) but only the $VSCN^{2+}$ and the $V(SCN)_6^{3-}$ appear to be stable in water, the latter only at high concentrations of thiocyanate.

5. Chelate Complexes of Vanadium

Many β- diketones and other organic materials have been used to form chelate complexes of metallic ions. These chelate compounds have, in general, found wide application in analytical and radiochemistry. They have been used as the basis for gravimetric, solvent extraction, and ion exchange methods of separation. The major consideration in this section is given over to the precipitation reactions of vanadium chelate complexes. Solvent extraction and ion exchange applications are discussed separately in subsequent sections.

Cupferron: The ammonium salt of N-nitrose-phenylhydroxylamine has been used widely as an analytical reagent. It was used originally (34) for the separation of copper and iron from numerous other elements (hence the name "cupferron"). It forms insoluble chelate precipitates with a large number of ions, especially those that yield trivalent and tetravalent hydroxide precipitates.

Cupferron dissolves readily in water, and is used most often as a six percent aqueous solution. Unfortunately, cupferron is somewhat unstable toward heat and light, nitrobenzene being the principal product formed in its decomposition. The reagent is best kept refrigerated in a brown bottle, with a stabilizing substance, such as phenacetin or acetophenetidine, added to improve stability.

Rodeja (35) has shown that acid solutions of the alkali metavanadates react with cupferron to produce a red precipitate which is somewhat soluble in water. Turner (36) found that vanadium, as the metavanadate, is separated completely from a solution containing uranium and one percent hydrochloric or sulfuric acid on adding aqueous cupferron. The precipitate can be ignited to produce vanadium pentoxide. The temperature at the time of precipitation must be kept below 20°, since higher temperatures cause a tarry mass to form, making filtration difficult or impossible. Too long a delay in removing the supernatant yields the same tarry mass. Vanadium cannot be separated from titanium or aluminum by this method (37).

Other ions which precipitate with cupferron from acid solution include iron (III), titanium (IV), zirconium, uranium (in 4-8 percent sulfuric acid), copper, gallium and aluminum; from weakly acidic solutions, bismuth, antimony (III), tin (IV), molybdenum (VI), thorium and tungsten also precipitate. The interferences of several of these elements can be eliminated by the use of the various complexing agents available, for example, ethylenediaminetetra-acetic acid. In order for vanadium to be precipitated quantitatively from any solution, it must be present in the tetravalent or pentavalent state. In highly dilute solution, iron (III) may be added as a collector (38) for vanadium if not already present in solution.

8-Hydroxyquinoline (Oxine): This versatile reagent was first introduced by Hahn (39) and Berg (40). It is very soluble in alcohol and acetic acid and forms insoluble chelate complexes with many metals. These complexes can often be dried at 105° to 140° C and weighed as such in gravimetric procedures.

Vanadium, as a vanadate, reacts with 8-hydroxyquinoline in the presence of acetic acid to form a yellow precipitate which changes color to blue-black on heating and cooling (41,42). The yellow compound is the hydroxyquinolate of tetravanadic acid:

$$(C_9H_7NO)_2 \cdot H_2V_4O_{11}$$

The blue-black compound is the anhydride of the acid

$$(C_9H_6NO) - V(OH) - (C_9H_6NO)$$

and has the composition

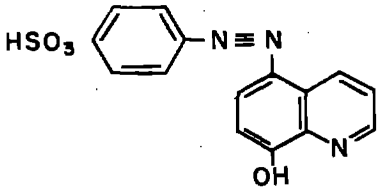
$$(C_9H_6NO)_2 = VO - O - VO = (C_9H_6NO)_2$$

The precipitation of vanadium with 8-hydroxyquindine is quantitative over the pH range 2.7 to 6.1 (43), hence the reagent can be used for the estimation of vanadium in the presence of calcium, cerium (III), chromium (III), gallium, magnesium, and palladium. Materials which can be expected to interfere with vanadium separation by 8-hydroxyquinoline are listed in Table IV (44-48).

Many of the interferences listed in Table IV can be eliminated by the use of masking agents. For example, by adding an excess of three percent hydrogen peroxide, most of the elements in Table IV can be precipitated, leaving vanadium in solution as the peroxy complex. Vanadium can then be precipitated, if desired, from dilute hydrochloric acid solution. (cf procedure 1 section VII).

<u>5,7-Dibromo-8-hydroxyquinoline</u>: This reagent has the same reactive group as 8-hydroxyquinoline, and thus reacts in a similar manner. It reacts with copper, titanium (IV), iron (II and III) and aluminum at pH 1.3-1.9. In 20-percent nitric acid, only iron (III) and vanadium (III) react (49), forming green and brown precipitates, repectively. The interference of ferric ion can be eliminated prior to vanadium precipitation by precipitating the iron with sodium hydroxide. Zirconium, cobalt and gallium also react with the reagent but in general, do not interfere with vanadium separation. The vanadium precipitate can be ignited to the oxide if oxalic acid is added prior to ignition.

<u>5-(p-Sulfophenylazo)-8-hydroxyquinoline</u>: When a



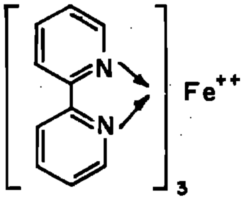
saturated alcoholic solution of this dye is added to a solution of a vanadate in 20-percent nitric acid, a brown precipitate is formed (50,51). Molybdenum (IV) and chromium (VI) must be absent as they form similar precipitates. Copper (II), mercury (II), nickel, and palladium also react.

Table IV. Elements Which Interfere in the Precpitation of Vanadium with 8-Hydroxyquinoline

Element	pH at which precipitation begins	Range through which precipitation is complete
Aluminum	2.8	4.2 - 9.8
Antimony	-	> 1.5
Bismuth	3.5	4.5 - 10.5
Cadmium	4.0	5.4 - 14.6
Cobalt	2.8	4.2 - 11.6
Copper	2.2	5.3 - 14.6
Indium	-	Acetic acid - sodium acetate
Iron(III)	2.4	2.8 - 11.2
Lead	4.8	8.4 - 12.3
Manganese(II)	4.3	5.9 - 10
Molybdenum	-	3.6 - 7.3
Nickel	2.8	4.3 - 14.6
Thorium	3.7	4.4 - 8.8
Titanium(IV)	3.5	4.8 - 8.6
Tungsten	-	5.0 - 5.7
Uranium	3.1	4.1 - 8.8
Zinc	2.8	4.6 - 13.4
Zirconium	-	Acetic acid - sodium acetate

<u>α, α' - Bipyridyl</u>: While the reagent alone does not react with vanadium to form a chelate complex, vanadium is precipitated nevertheless in the presence of the ferrous

ion (52). The reaction appears to take place between a ferrous-bipyridyl complex:



and the vanadate ion in neutral or weakly ammoniacal solution. Tin (IV), zinc, cadmium, tantalum (V), and niobium (V) also react.

<u>α-Nitrose-β-naphthol</u>: An alcoholic solution of this reagent, when added to an alkaline solution of ammonium metavanadate, produces a green coloration, followed by the separation of a brown precipitate (53). When the reaction is carried out in dilute acid solution, a large reddish precipitate forms. A similar reaction occurs between the reagent and a dilute solution of ammonium molybdate. Both precipitates are soluble in concentrated mineral acids.

Terrisse and Lorréol (54) have reported that the reagent does not precipitate vanadium quantitatively. Bellucci and coworkers (55), however, claim complete precipitation.

Tanii, <u>et al</u>. (56) give the data listed in Table V for the effect of pH on the precipitation of several metals with α-nitroso-β-naphthol.

Table V. Suitable pH Ranges For The Precipitation of Metals With α-Nitroso-β-naphthol

Metal	pH Range
Cobalt	< 8.74
Copper	3.96 - 13.2
Iron	0.95 - 2.00
Vanadium	2.05 - 3.21
Palladium	< 11.82
Uranium	4.05 - 9.38

Salicylaldoxime: This reagent has been used in forming chelate complexes of many metals. The data of Jean (57) indicates that vanadium, as VO_3^-, forms a black precipitate with salicylaldoxime in acid solution. Jean lists the optimum range of acid concentration for precipitation as 0.05 - 1.0 N, but notes that at best only 60-70 percent of the vanadium is precipitated. Copper (II) and palladium (II) also react in acid solution, forming yellow to yellow-green precipitates. Iron (III) interferes also, but molybdenum and chromium do not (58).

Acetylacetone (2,4 - Pentanedione): Vanadium (III, IV, and V) form chelate complexes with this material. Little information has appeared in the literature concerning precipitation reactions involving acetylacetone, possibly as a result of the water solubility of many of the chelate complexes, and of the reagent itself. In addition, many of the complexes are soluble in an excess of the reagent. However, in a study by Jones (59), the vanadyl chelate was prepared by dissolving the ligand in ethanol, adding the alcoholic solution to solution of vanadyl ions in dilute sulfuric acid, and neutralizing with 10-percent sodium carbonate solution. The resulting vanadyl-bis-acetylacetonate settles to the bottom as an oil which slowly solidifies. The monohydrate of this chelate is water insoluble. When its solution in ether is boiled with ammonia or an amine, the water of hydration is replaced to give $VOA_2 \cdot B$, where A is the ligand and B the base.

The acetylacetone chelates of vanadium appear to form most readily in acid solution; a pH of 2.3 or greater for vanadium (III and IV), and a pH between 1.8 and 2.4 for vanadium (V) appear to be optimum. Interferences under these conditions include iron (III), titanium (IV), molybdenum (VI), chromium (III), aluminum, copper, cobalt, and small amounts of manganese (II) and zirconium (IV).

N-Benzoylphenylhydroxylamine: This reagent, having a structure closely resembling that of cupferron, also resembles cupferron closely in its analytical reactions. Unlike cupferron, however, it is quite stable toward heat, light, and air. It forms water insoluble chelate complexes with tin, titanium, zirconium, vanadium (V), molybdenum (VI), and tungsten (VI) in acid solution. Copper, iron, and aluminum precipitate at a pH of approximately 4.0, while cobalt, cadmium, lead, mercury, manganese, uranium, and zinc react at pH values greater than 4.0 (60-61). The vanadate chelate complex precipitates as an orange-red mass, insoluble in water, but soluble in benzene, ethanol or acetic acid (62).

3-Hydroxyl- 1,3-diphenyltriazine: This reagent (63) has the following useful properties: it is stable to heat, light, and air, and is capable of being stored indefinitely. Its chelate complexes with many metals are granular, water insoluble, stable thermally, and may be suitable for direct weighing. Below pH 3 it forms chelate precipitates only with copper, palladium (II), iron (II, III), vanadium (III,V), titanium (IV), and molybdenum (VI). Except for the copper and palladium chelates, the precipitates are decomposed on heating in acid solution.

Vanadium forms chelate complexes with several other organic ligands; ethylenediaminetetra-acetic acid and 1,2-diaminocyclohexane-N, N, N', N'-tetra-acetic acid chelate complexes with vanadium (II, III, and IV) have been reported. (64, 65). In addition, glycollic acid (66) potassium xanthate (67), and sodium diethyldithiocarbamate (68) all give precipitates with vanadium salt solutions, and have been used to some extent in analytical schemes.

6. Extraction of Thenoyltrifluoroacetone Complexes of Vanadium into Organic Solvents

A survey of the literature indicates that little or no interest has been shown in the chelation and extraction of vanadium by means of thenoyltrifluoroacetone. It appears that the only information available on this extraction is that obtained in the laboratories of the Nuclear Chemistry Group at the University of Michigan (69).

Extraction of vanadium by means of its TTA complex was undertaken using 0.25 M solution of TTA in benzene. Equal volumes of the benzene solution of the ligand and carrier solution (10 mg vanadium per ml.) were shaken together for one minute. The extraction of the vanadyl-TTA complex as a function of pH is shown in Figure 1, from the data of

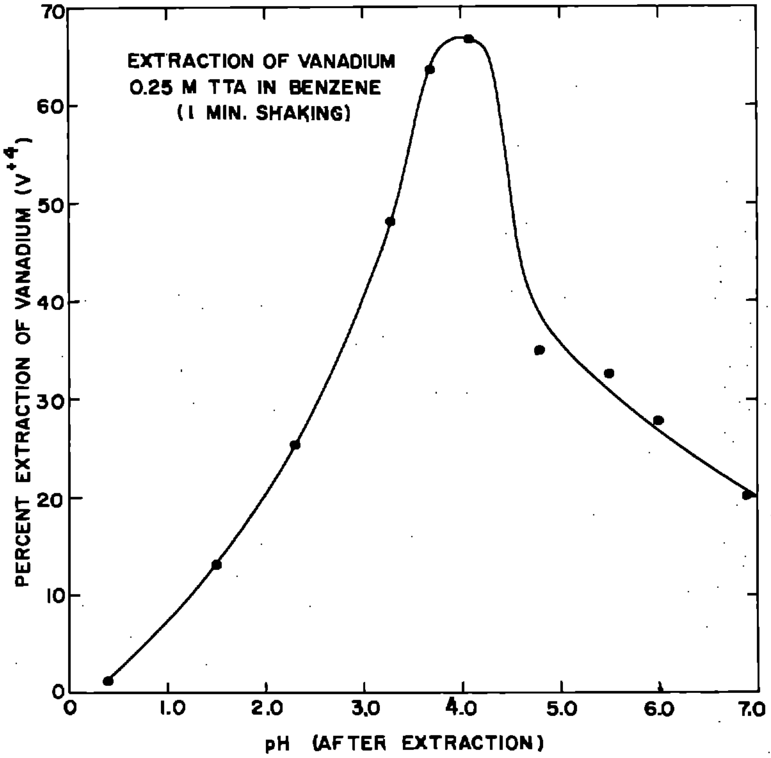


Figure 1 Extraction of Vanadium (IV) into TTA.

Fukai (69). A comparison of vanadyl-TTA extraction with other chelates has been abstracted by Shepard and Meinke (70). The vanadium can be back-extracted by shaking the benzene solution with an equal volume of 1-N hydrochloric acid with 99-percent recovery.

The extraction of pentavalent vanadium proceeds much more slowly than in the case of the quadrivalent state. Only very small amounts of vanadium were extracted after continuous shaking for several hours, and further experiments were cancelled.

7. Extraction of Vanadium into Organic Solvents

The following discussion is divided into two major catagories: A, The extraction of ion-association (i.e. inorganic complex) systems, and B, The extraction of chelate-complexes.

A. Ion Association Systems

1. Chlorides: Vanadium (V) is only partially extracted into isopropyl ether from hydrochloric acid solutions. Dodson, et al (71) have reported that only 22-percent of the vanadium present in 7.75-M HCl solution is extracted into isopropyl ether when 250 mg. of vanadium (V) are present in solution. They have found a 43-percent extraction along with ferric ion when the solution contains 48.5 mg. of vanadium (V) and 500 mg. of iron (III).

   Under conditions essentially the same as those above, vanadium (IV) extracts into isopropyl ether to the extent of less than 0.08-percent from a solution containing 258 mg. of vanadium (IV), and approximately 0.4-percent from a solution containing 51.5 mg. of vanadium (IV) and 500 mg. of iron (III).

Other elements which extract as well as the chloride complexes into organic solvents include Sb(V), As(III), Ga(III), Ge(IV), Au(III), Fe(III), Hg(II), Mo(VI), Nb(V), Pt(II), Po(II), Pa(V), Tl(III) and Sc(III). Elements only partially extracted include Sb(III), As(V), Co(II), In(III), Te(IV), Sn(II) and Sn(IV).

2. <u>Fluorides</u>: Relatively few studies have been made on the extraction of the fluoride complexes of metals. In part, this has been a result of the difficulty in the handling of solutions of hydrofluoric acid, requiring the use of plastic laboratory ware. However, Bock and Herrmann (72) have reported extensively on the extraction of many metals as fluoride complexes into such solvents as n-pentanol, methylisobutyl ketone, ethyl ether, di-n-butyl ether, amyl acetate, nitrobenzene, and anisole.

   Bock and Herrmann report the extraction of 12-percent of the vanadium (III) and 8.5-percent of the vanadium (V) into ethyl ether from 20-<u>M</u> hydrofluoric acid solution. Certain of their data are presented in Figure 2.

3. <u>Bromides</u>: An extensive study of the distribution of metal bromides between certain of the organic solvents mentioned above and solutions of hydrobromic acid at varying concentrations has been conducted by Bock, Kusche, and Bock (73). They found that Au(III), Ga(III), In(III), Tl(III), Sb(V), Sn(II), Sn(IV), and Fe(III) extract well into ethyl ether. As(III), Sb(III), Se(IV), and Mo(VI) extract to a lesser extent, while only

slightly extracted are Cu(II) and Zn. Approximately 1×10^{-3} percent of vanadium (IV) is extracted into ether at hydrobromic acid concentrations of one-and-six-molar. No information is available for other HBr solutions.

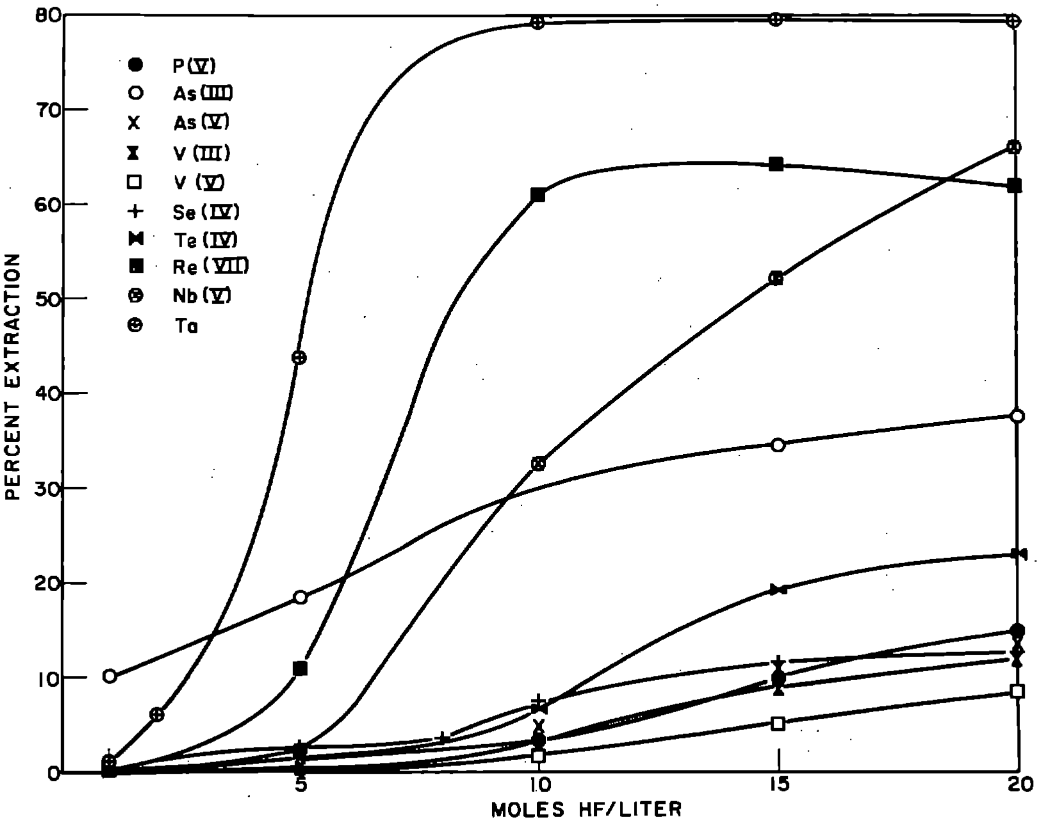


Figure 2. Distribution of fluorides between HF solution and ethyl ether.

4. <u>Thiocyanate</u>: Alkali thiocyanates have long been used in the colorimetric estimation of many metals. Complexes with thiocyanate are formed by iron (III), uranium (VI), bismuth, niobium, and rhenium, as well as cobalt (II) and ruthenium (III); these can be extracted readily into oxygen-containing organic solvents. In the presence of reducing agents and/or

masking agents, tungsten, molybdenum, nickel, and copper also form extractable thiocyanate complexes.

The work of Bock (74) has revealed that Be, Zn, Co, Se, Ga(III), In(III), Ti(III), Fe(III), Sn(IV), and Mo(VI) are extracted readily into ethyl ether. Aluminum, V(IV) and U(VI) extract to a lesser extent; Li, Cu, Cd, Hg(II), Ge, As(III), As(V), Sb(III), Bi, Cr(VI), Ni, and Pd are extracted only slightly. Certain of the extraction data for these ions appear in Figure 3.

The results of the investigations of Bock (74) show that although Be, Zn, Ga(III), Fe(III), Sc, U(VI), and V(IV) can be extracted from neutral solutions at their particular optimum thiocyanate concentrations, the extraction of most of these is more favorable at a hydrochloric acid concentration of 0.5 molar in the aqueous phase.

The behavior of the system; Mn(II)-V(IV)-Cr(III)-SCN^--Methylisobutyl ketone has been studied by Lemmerman and Irvine (75) in preparing a separation of V^{48} from deuteron-irradiated chromium foil or chromic acid targets (procedure 8, Section VII). Their results are summarized in Table VI (75).

5. Nitrates: Several investigators (76-78) have reported that small amounts of vanadium are transferred to the organic phase in the system: vanadium-nitric acid-ethyl ether. Results of a study by the Princeton Analytical Group (76) involving the extraction of impurities in an ethyl ether-nitric acid system show the distribution coefficients (organic/aqueous) for vanadium (V) in 3-N and 5-N nitric acid to be 0.004

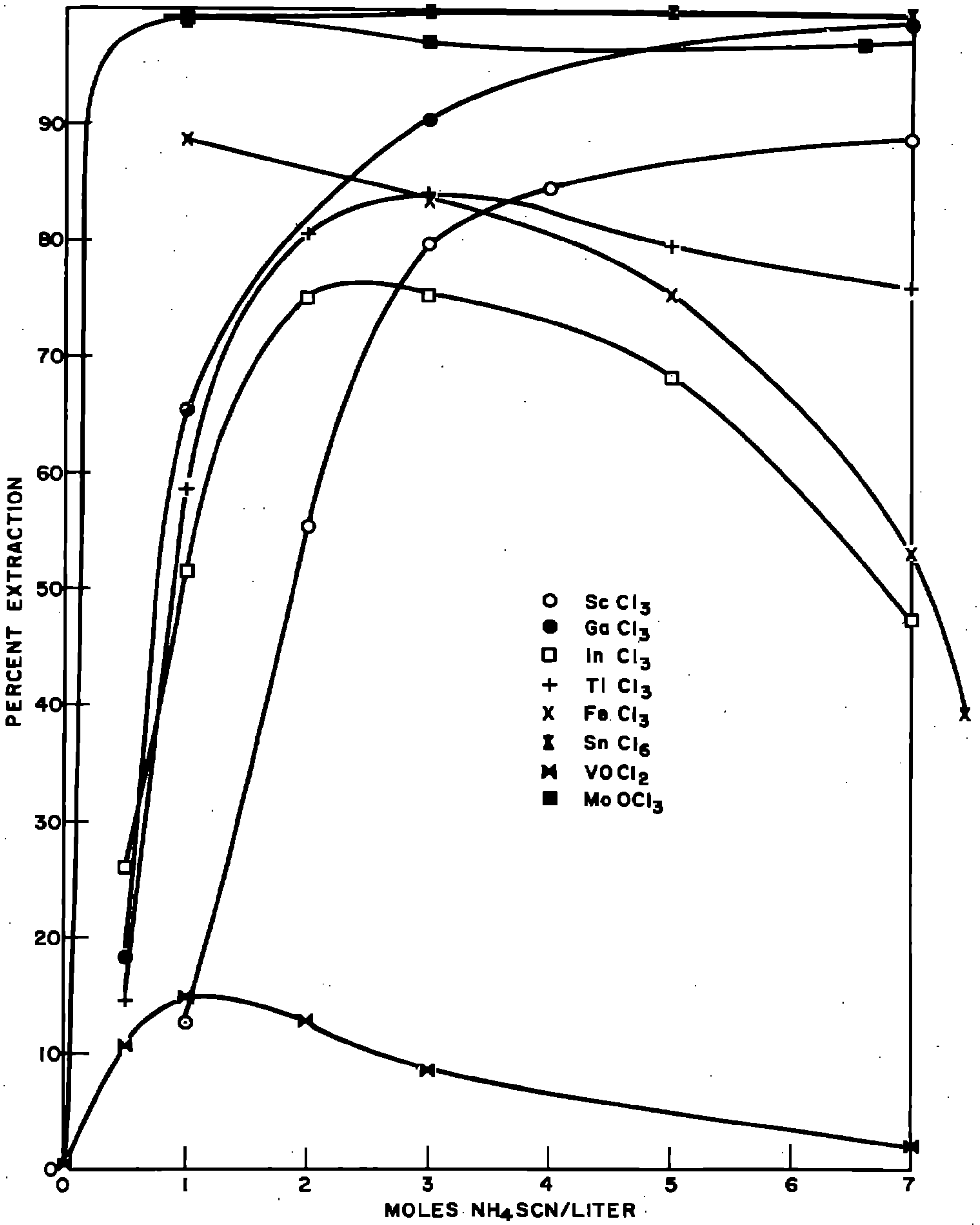


Figure 3 Extraction of Thiocyanates into Ethyl Ether.

Table VI. Summary of the Extraction of Mn(II) and V(IV) into MiBK

Range of Variable	Constants*	Range K_dMn(II)	Range K_d V(IV)
0.94 - 7.6 f KSCN	ah	3.6×10^{-2} - 25.0	
	bh		2.2 - 36.3
	ach	7.7×10^{-2} - 16.8	
	bch		31.2 - 114
pH 3-12	ace	7.1×10^{-3} - 18.6	
pH 2-12	bce		18 - 8.3×10^{-3}**
pH 3-12	acd	3.3×10^{-2} - 5.1	
pH 2-12	bcd		122 - 6.2×10^{-2}
pH 3-11	ae	1.3×10^{-2} - 4.8	
pH 3-11	be		2.6 - 4.2×10^{-3}
pH 4-11	ac	1.4×10^{-4} - 1.9	
pH 3-10	bc		1.6 - 3.2×10^{-3}
9.1×10^{-2} - 7.5×10^{-7} f Mn(II)	gh	1.5 - 11	
7.3×10^{-2} - 3.1×10^{-7} f V(IV)	fh		5.1 - 6.6
9.9×10^{-2} - 7.5×10^{-7} f Mn(II)	cgh	3.0 - 8.9	
7.0×10^{-3} - 3.1×10^{-7} f V(IV)	cfh		18 - 42

* a = 7.5×10^{-7} f Mn(II)
b = 3.0×10^{-7} f V(IV)
c = 1.3×10^{-2} f 8-HQ
d = 1.0 f KSCN
e = 2.0 f KSCN
f = 4.0 f KSCN
g = 6.2 f KSCN
h = pH 7

** Max. 33 at pH 7; at 1.3 M OH^- K_d fell to 0.3

and 0.016, respectively (79). Distribution coefficients for vanadium (IV) were found to be somewhat lower.

As a result of interest in uranium-bearing ores, many of which contain varying amounts of vanadium, it has been found that vanadium (V) can be extracted in yields up to 95-percent from nitric acid solutions in the pH range 1.5-2.0 using 0.6-molar solutions of tri-n-octylphosphine oxide in Kerosene. Sulfate and carbonate ions tend to retard the extraction, while chloride appears to have no effect. Inasmuch as vanadium (IV) is not extracted appreciably, the vanadium can be stripped from the organic phase by contacting with a reducing agent, such as 0.25 molar oxalic acid solution. Further data on such extractions may be found in recent Atomic Energy Commission reports (e.g., 80-82), and techniques and procedures (e.g. 83).

6. Heteropoly Acids: A characteristic property of heteropoly acids is their solubility in organic slovents. Elements capable of forming this type of complex include Mo, As, P, W, V, and Si.

   For the most part, esters, ketones, aldehydes, and ethers are good extractants for heteropoly acids (84). Carbon disulfide, carbon tetrachloride, chloroform, benzene, and toluene do not make good extractants for heteropoly acids (85).

   Molybdovanadophosphoric acid has been found (86,87) to be extractable into mixtures of 3-methyl-1-butanol and ether, 1-butanol and ether or isobutyl acetate; 1-butanol, and ethyl ether.

In addition to the above extractions of vanadium complexes, vanadium can also be extracted from aqueous solutions by relatively high molecular weight amines and by alkylphosphoric compounds. A great wealth of material on these compounds can be found in recent literature (e.g., 88-96).

B. Chelate Systems

Many, if not all, of the chelate complexes considered in section 5 can be extracted into organic solvents. Several of these chelate systems are discussed below.

Cupferron: The chelate precipitate of vanadium (V) and cupferron has been found to be soluble in a variety of organic

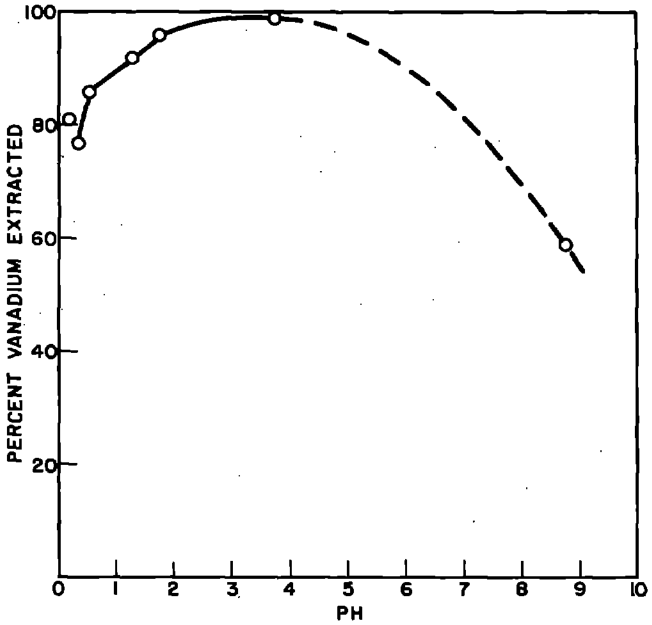


Fig. 4. Extraction of Vanadium (V) Cupferrate into Chloroform from H_2SO_4 Solution.

solvents, including ethyl acetate, ether, carbon tetrachloride, and chloroform. Certain of the chelates formed with other metals are soluble in toluene, methyl ethyl ketone, butyl acetate, and benzene. Furman, Mason, and Pekola (97) have carried out a rather extensive study of cupferron separations and consider extraction of the chelates to be superior by far to precipitation techniques for separation of microgram to milligram amounts of metal ions.

The dependence upon pH of the cupferron extraction of vanadium (V) from dilute sulfuric acid solution is given in Figure 4 (98). Equal volumes (100 ml.) of aqueous solution and chloroform were shaken together for several minutes in obtaining these data. The extraction of vanadium (IV)-cupferrate from hydrochloric acid solution into ethyl acetate is presented in Figure 5 (99) as a function of pH. Table VII (100) gives data on the extractability of several metal cupferrates into various organic solvents.

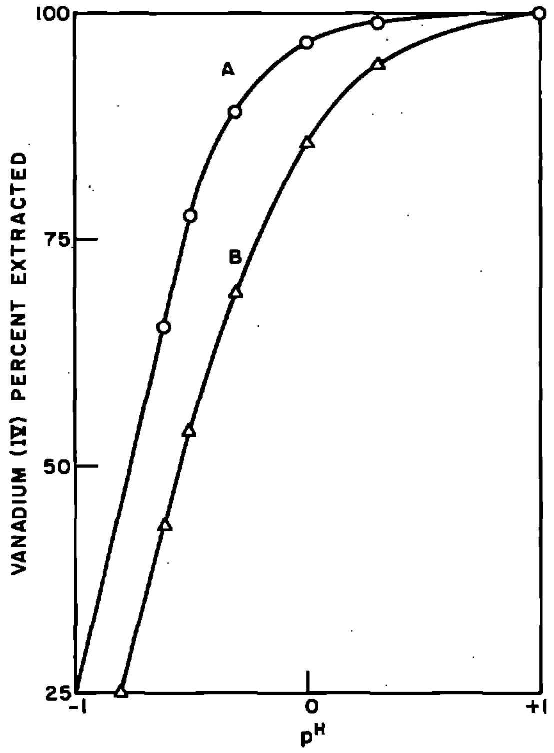


Fig. 5. Extraction of Vanadium (IV) Cupferrate into Ethyl Acetate from HCl Solution. Cupferron Concentration in Organic Phase: Curve A, 9×10^{-2} M; Curve B, 6×10^{-2} M.

Table VII. Extraction of Metal Cupferrates (100)

Z	Element	Extraction Range	Solvent
13	Al	pH 2-5	Chloroform
22	Ti (II)	pH $\sim$ -0.08	Chloroform, ether, ethyl acetate
23	V (V)	pH -0.08 to -0.56	Chloroform, ether, ethyl acetate
25	Mn (II)	pH $\sim$ 7	Ether
26	Fe (III)	pH $\sim$ -0.56	Chloroform, ether, ethyl acetate
27	Co	dilute HOAc	chloroform, ether, ethyl acetate
28	Ni	pH $\sim$ 7	Organic solvents
29	Cu (II)	pH $\sim$ 0.08	Chloroform
30	Zn (IV)	pH $\sim$ 7	Ether (extraction incomplete)
40	Zr (IV)	pH $\sim$ -0.56	Ethyl acetate
41	Nb (V)	pH $<$ 7	Chloroform
42	Mo (VI)	pH $\sim$ -0.35	Chloroform, ethyl acetate
48	Cd	pH $\sim$ 7	Boiling ether
49	In	dilute acid	Chloroform, benzene
50	Sn (II)	pH $\sim$ -0.18	Chloroform, benzene
50	Sn (IV)	pH $\sim$ -0.08	Ethyl acetate
51	Sb (III)	pH $\sim$ -0.56	Chloroform
58	Ce (IV)	pH 2	Butyl acetate
74	W (VI)	pH $\sim$ -0.08	Ethyl acetate (extraction incomplete)
80	Hg (II)	pH $\sim$ 7	Chloroform, benzene
83	Bi	HCl or H_2SO_4	Toluene, methyl-ethyl ketone
90	Th	pH $\sim$ -0.08	Ethyl acetate, butyl acetate
91	Pa	pH or 4 N HCl	Chloroform, ether, benzene
92	U (IV)	pH $\sim$ -0.56	Ether

8-Hydroxyquinoline (Oxine): This reagent is somewhat sensitive to light and heat. It is generally used as a 1-percent solution in chloroform, or as a 5-percent solution in acetic acid. Extraction can be made of the metal chelate complexes into several of the more commonly used organic solvents. Talvitie (101) extracted the vanadium chelate into chloroform from a phthalate buffer at pH 4. Bach and Trellers (102) extracted vanadium 8-hydroxyquinolate into isoamyl alcohol to obtain a red solution.

As shown by Table VIII (100), 8-hydroxyquinoline extraction of vanadium is subject to interference by many ions. However, by suitable buffering and the use of masking agents, much of this interference can be eliminated. It should be noted, however, (see Procedure 1, Section VII) that the presence of hydrogen peroxide precludes extraction of vanadium (V) 8-hydroxyquindate into organic solvents because of the formation of a vanadium peroxy complex.

Acetylacetone (2,4-Pentanedione): This reagent is somewhat unique among chelate-forming compounds inasmuch as many of the metal chelates formed are soluble in an excess of the reagent. In general, the solubilities of many of the acetylacetone chelates are of the order of a magnitude or more higher than the solubilities of most other chelates.

Table IX (100) presents information on the extractability of several metals with acetylacetone. As in the case of cupferron and 8-hydroxyquinoline, masking agents and close control of pH can lead to satisfactory separations. Figure 6, compiled from the data of McKaveney (103), shows the extraction of several metal-acetylacetonates as a function of pH.

N-Benzoylphenyl hydroxylamine: The vanadium (V) chelate with this reagent is soluble in benzene (104).

Table VIII. Extraction of Metals with 8-Hydroxyquinoline (100)

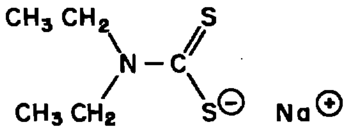
Z	Element	Optimum Extraction Conditions	Solvent
12	Mg	pH 10.2	Butyl cellosolve, chloroform
13	Al	pH 4.8-6.7;8.2-11.5	
20	Ca	pH 13	Butyl cellosolve, chloroform
21	Sc	pH 6.5-8.5	
22	Ti (IV)	pH 3.8-5.0	
23	V (V)	pH 3.3-4.5	Chloroform, isoamyl alcohol
25	Mn (II)	pH 7.2-12.5	Tartrate used at high pH
26	Fe (III)	pH 1.9-12.5	Tartrate used at high pH
27	Co	pH >6.8	
28	Ni	pH 4.5-9.5	
29	Cu (II)	pH 2.8-14	Tartrate used at high pH
30	Zn	pH 4.6-13.4	extraction incomplete
31	Ga (III)	pH 3.0-6.2	
38	Sr	pH 11.28	1 *M* 8-hydroxyquionline in chloroform
40	Zr (IV)	HOAc-acetate buffer	
41	Nb (V)	pH ~ 11.63	citrate used at high pH
42	Mo (VI)	pH 1.6-5.6	
44	Ru (III)	Acetate medium	
46	Pd	Dilute HCl	
48	Cd	pH ~ 8	Extraction incomplete
49	In (III)	pH >3.0	
50	Sn (IV)	pH 2.5-5.5	
58	Ce (III)	pH 9.9-10.5	
60	Nd	pH > 8.5	
68	Er (III)	pH >8.5	
74	W (VI)	pH 2.4-4.3	
81	Tl (III)	pH 6.5-7.0	85-89% extraction
82	Pb	pH 8.4-12.3	
83	Bi	pH 4.0-5.2	
90	Th	pH 4.9	Chloroform, methyl isobutyl ketone
91	Pa	Sat'd. $(NH_4)_2CO_3$	Extraction incomplete
92	U (VI)	pH 4.7-8.0	
94	Pu (IV)	pH 4 - 8	Amyl acetate
94	Pu (VI)		

Table IX. Extraction of Metal-Acetylacetone Chelates (100)

Z	Element	Optimum Extraction Conditions	Solvent
4	Be	pH 2	Acetylacetone
4	Be	pH 5-10	Benzene
13	Al	pH 4	Acetylacetone
22	Ti (IV)	pH 1.6	Acetylacetone + chloroform (~76% extracted)
23	V (III)	pH 2.0	Acetylacetone + chloroform (~93% extracted)
	V (IV)	pH 2.5	Acetylacetone (73% extracted)
24	Cr (III)	pH 0.0-2	Acetylacetone + chloroform
25	Mn (II)	pH ~ 4	Acetylacetone
26	Fe (III)	pH 1.5	Acetylacetone
27	Co (III)	pH -0.3 to 2.0	Acetylacetone
29	Cu	pH 2.0	Acetylacetone
30	Zn	pH 5.5-7.0	Acetylacetone (~70% extracted)
31	Ga (III)	pH 2.5	Acetylacetone
40	Zr (IV)	pH 2-3	Acetylacetone (~73% extracted)
42	Mo (VI)	pH -0.8 to 0.00	Acetylacetone + chloroform
49	In (III)	pH 2.8	Acetylacetone
58	Ce	pH > 4	Acetylacetone
90	Th	pH 5.8	Benzene
92	U (VI)	pH 4-6	Acetylacetone
94	Pu (IV)	pH 2-10	Benzene

Benzohydroxamic Acid: This reagent forms a water-soluble colored chelate complex with vanadium (V). Bhaduri (105) found that the chelate can be extracted into certain oxygenated organic solvents, such as 1-pentanol, hexanol, amyl acetate; isobutyl acetate has also been used (106).

Sodium Diethyldithiocarbamate: A 2-percent aqueous sloution of this reagent has been used widely in metal-chelate extractions. Having the structure



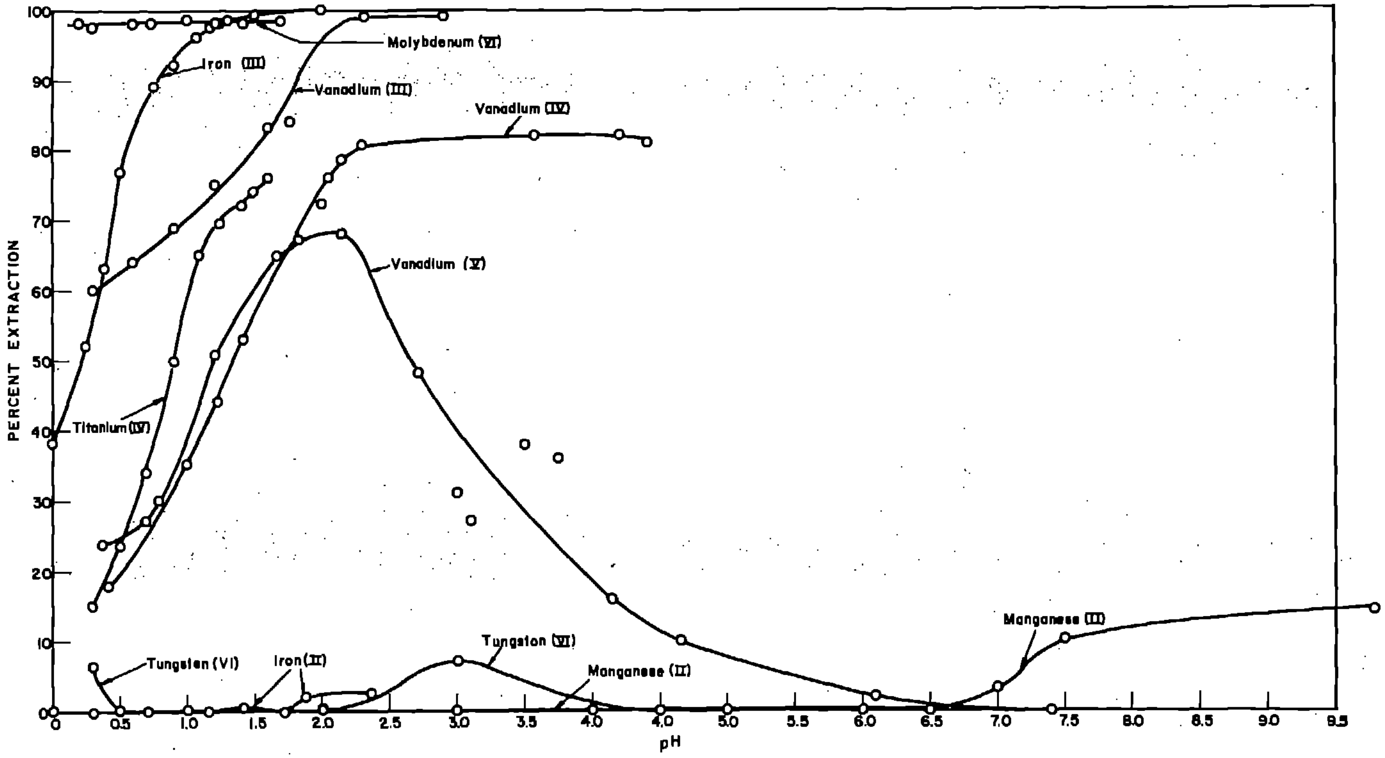


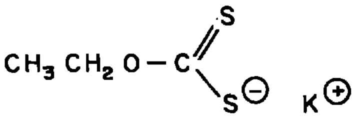
Fig. 6. Extraction of Acetylacetonates as a Function of pH (103).

the reagent is water soluble. The chelates, however, are soluble in such solvents as chloroform, carbon tetrachloride, ether, amyl acetate, benzene, and ethyl acetate. Extractions possible with the reagent are given in Table X (100). It has been found (107) that the reagent decomposes quite rapidly in solutions of low pH. Extractions carried out at these low pH's should be performed using an excess of reagent to affect decompostion.

Table X. Extraction of Diethyldithiocarbamate Chelates (100)

Z	Element	pH Range for Optimum Extraction	Solvent
23	V	3	Ethyl acetate
24	Cr (VI)	0-6	Chloroform
25	Mn (II)	6.5	Ethyl acetate
26	Fe (II)	4-11	Carbon tetrachloride
26	Fe (III)	0-10	Chloroform
27	Co	6-8	Chloroform
28	Ni	0-10	Chloroform
29	Cu	1-3.5	Chloroform
30	Zn	3	Ethyl acetate
31	Ga	3	Ethyl acetate
33	As (III)	4-5.8	Carbon tetrachloride
34	Se	3	Ethyl acetate
41	Nb (V)	Weakly acid	Carbon tetrachloride
42	Mo (VI)	3	Ethyl acetate
47	Ag	3	Ethyl acetate
47	Ag	4-11	Carbon tetrachloride
48	Cd	3	Ethyl acetate
49	In	3	Ethyl acetate
50	Sn (IV)	5-6	Carbon tetrachloride
51	Sb (III)	4-9.5	Carbon tetrachloride
52	Te (IV)	5 N H^+; pH 3.3 8.5-8.7	Chloroform, benzene Carbon tetrachloride
74	W (VI)	1-1.5	Ethyl acetate
75	Re	12.2 N HCl	Ethyl acetate
76	Os	7-9 (slow; extraction incomplete)	Carbon tetrachloride
80	Hg	3	Ethyl acetate
81	Tl	3	Ethyl acetate
82	Pb	"very acid"	Ether, ethylacetate
83	Bi	1-10	Chloroform, ether
92	U (VI)	6.5-8.5	Chloroform, ether, amyl acetate

Potassium Xanthate: This reagent, having the structure



is formed by the action of alcohol on carbon disulfide in alkaline medium. The aqueous solution is quite alkaline, and reacts with the metals listed in Table XI (100), forming metal chelates capable of being extracted into certain organic solvents.

Table XI. Extraction of Xanthate Chelates (100)

Z	Element	Conditions for Optimum Extraction	Solvent
23	V (V)	pH ~ 3-7	Chloroform
26	Fe	pH ~ 3-7	Chloroform
27	Co	Ammoniacal solution	Ether
28	Ni	pH ~ 3-7	Chloroform
29	Cu	pH 7-8.5 or ammoniacal solution	Ether
33	As	Acid solution	Carbon tetrachloride
42	Mo (VI)	pH ~ 3-7	Petroleum ether and ether or chloroform
51	Sb	Acid solution	Carbon tetrachloride
52	Te	Thiourea solution	Ether
92	U	pH ~ 3-7	Chloroform

It is quite probable that several of the vanadium chelates not included in the above discussion can be applied to the solvent extraction of vanadium from various solutions. However, information on the solubilities of these chelates appears not to be available in the literature.

8. Ion-Exchange Behavior of Vanadium

Several very good works on ion exchange techniques and procedures have been published in recent years. Austerweil (108) and Eeckelaers (109) have written books in French on the general aspects of ion exchange. Two American texts are those of Samuelson (110) and the works edited by Nachod and

Schubert (111). These give procedures for many separations, as well as a discussion of the theory and techniques involved in ion exchange. Osborn (112) has compiled a useful bibliography in which the ion exchange behavior of the elements has been segmented. More recent reviews are those of Kraus and Nelson (113), and Kunin, McGarvey, and Fabian (114). Kunin and Preuss (115) have reviewed the extensive use of ion exchange techniques in the field of atomic energy, while Martinez (116) and Schultz (117) have summarized analytical procedures using ion exchange techniques.

A method for the separation of rhenium from vanadium and tungsten has been published by Ryabchikiv and Lazaryek (118) in which the rhenium is separated from vanadium by passing the two ions in 0.3 N hydrochloric acid through an anion exchange column of MMG-1 in the hydroxide form. The vanadium is eluted with 0.3 N hydrochloric acid; rhenium is then removed from the column with 2.5 N sodium hydroxide. Separation of these two elements can also be effected by passing a (neutral) solution of the ions through a column of SBS cation exchange resin in the hydrogen form. The rhenium is eluted with dilute acid; vanadium is eluted with 1:4 ammonium hydroxide. A separation of vanadium from tungsten involves adsorption of these ions at pH 1 on a column of anion-exchanging aluminum oxide, with elution of the vanadium by means of a solution containing hydrogen peroxide at pH 1. Tungsten is eluted with a solution of amonium hydroxide.

A rather unusual procedure for the separation of uranium and vanadium in carbonate leach liquors has been developed by Saunders (119), and involves the electrolytic precipitation of uranium in a solution 1 M in sodium carbonate. An electrolytic cell of plexiglass is divided into two portions by an ion exchange membrane which permits the passage of cations only. The uranium-and vanadium-bearing leach liquor is placed in one portion of the cell, and the sodium carbonate solution in the other. A direct current is applied, and the uranium precipitates as U_3O_8 and/or UO_2 in the portion of the cell containing the sodium carbonate. The vanadium remains in the leach liquor solution and can be removed from solution by electrolysis at an amalgamated lead cathode.

Murthy (120) has also investigated the separations of vanadium and uranium by ion exchange methods in sodium carbonate solution. A solution containing uranium, as the carbonate complex $[UO_2(CO_3)_3]^{4-}$, and vanadium, as VO_3^-, in excess sodium carbonate is passed through a column of Amberlite IRA-400 anion exchange resin in the chloride form. All of the uranium, and part of the vanadium is adsorbed on the column. The vanadium is eluted with a 10-percent solution of sodium carbonate. The uranium is desorbed with a sodium chloride solution. The elution of vanadium with sodium carbonate is shown in Figure 7.

Erlenmeyer and Dahn (121) have investigated the use of 8-hydroxyquinoline as an adsorption agent in the chromatographic separation of several ions, in which the adsorption takes place by means of chelate formation. The order of adsorption, and the color of the various layers formed has been given as:

1. VO_3^- : grayish-black
2. WO_4^{2-} : yellow
3. Cu^{2+} : green
4. Bi^{3+} : yellow
5. Ni^{2+} : green
6. Co^{2+} : pink
7. Zn^{2+} : yellow, with intense green fluorescence
8. Fe^{3+} : black
9. UO_2^{2-} : reddish-orange

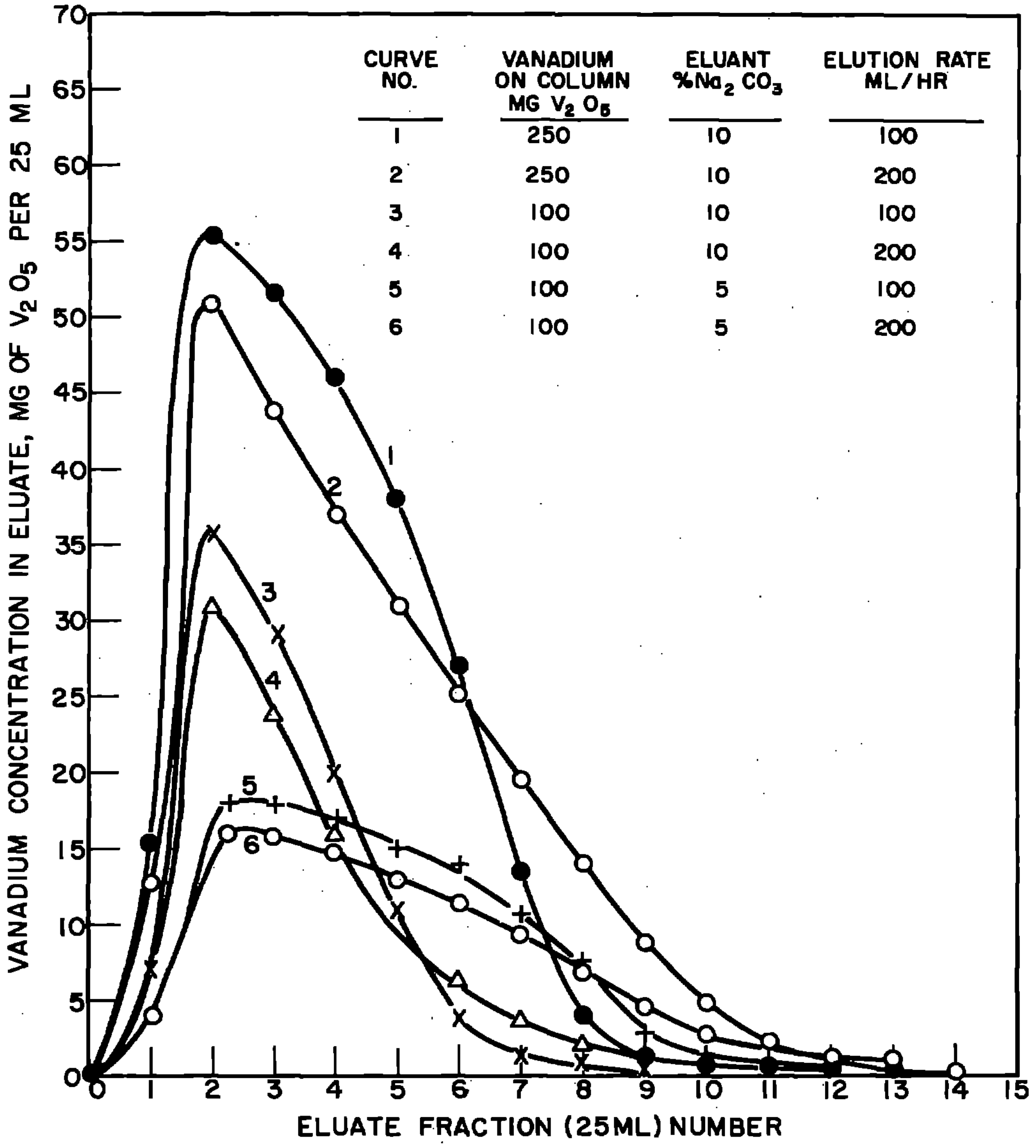


Figure 7.Elution of Vanadium(V) from IRA-400 with sodium carbonate.

It would appear that the order of adsorption corresponds well to the order of solubilities of the 8-hydroxyquinolates. However, the order of adsorption is somewhat dependent upon pH; the order of adsorption of zinc and iron is reversed in acetic acid solution. The most obvious disadvantage of this type of separation lies in the restrictions placed on types of solutions which can be used. Systems which attack or dissolve the adsorbant cannot be used. However, this type of technique points the way toward the use of other chelate-forming adsorbants where resin exchangers may be ineffective.

Hicks and co-workers (122) have investigated the behavior of a number of metals toward anion exchange on Dowex-2, a strong basic type of resin. The resin is converted to the chloride form by treatment with concentrated hydrochloric acid before use, and is slurried into a column arrangement such that a bed of resin approximately 10 cm. long by 0.4 cm. in diameter is deposited. The elements to be studied are placed on the column in concentrated hydrochloric acid; approximately 0.1 to 0.4 milliequivalents (~ 10 mg) of each metal is used. The solution is passed through the column at a rate of one drop every 5 to 10 seconds. When the liquid is nearly level with top of the resin, a drop of concentrated hydrochloric acid is added to the reservoir. The liquid is passed through until the level again approaches the top of the column, and two additional ml of concentrated hydrochloric acid are added as a wash. On completing this wash, which represents approximately five free column volumes, the eluate is checked for the metal being studied. If the metal is not eluted by this procedure, 4-ml. of 9 M HCl are passed through the column, and the eluate rechecked. Hydrochloric acid of 6, 3, 0.1 and 0.001 molarity is then tried in succession until the metal appears in the eluate. Water, 3 M perchloric acid, molar ammonium hydroxide, and finally, molar sodium hydroxide are used as eluants if the hydrochloric acid does not remove the metal from the column. If 4 ml. of eluant do not remove the metal completely from the column (approximately 10 column volumes), the metal is considered not to be eluted by the particular eluant.

The results of this investigation are presented in Table XII, which lists only those elements investigated. Note that vanadium (II, III and IV) are eluted with concentrated hydrochloric acid, signifying very slight adsorption of these ions on the column. Vanadium (V), on the other hand, is adsorbed from concentrated hydrochloric acid, and is eluted, along with Ti (IV), Pt (II), Zr (IV), Hf, and trace amounts of Ag and Ta, by 6-9 M HCl.

In the summary of results in Table XII, it is well to note that elements which are eluted by a given eluant have, in general, rather widely different chemical properties. Subsequent separation of these elements can then be accomplished by other methods.

Studies similar to that of Hicks, et al., have been conducted by Kraus and Nelson (123) and Kraus, Nelson and Smith (124). Kraus and Nelson studied the adsorption of a number of metal ions in hydrochloric acid on Dowex-1 anion exchange resin. They found that over the range 1-12 M hydrochloric acid no region is found where considerable adsorption takes place for vanadium (IV). In

Table XII. Elution of Elements from Dowex-2
Anion Exchange Resin (122)

Eluting Agent	
12 M HCl	Alkali metals, alkaline earths, rare earths, Sc, Y, Ti (III), V (II, III, IV), Ni, As (III), As (V), Se (IV), Tl (I), Pb, Bi, Cu (II) slowly, Al, Cr (III), Fe (II), Mn (II)
6-9 M HCl	Ti (IV), V (V), Ag*, Ta*, Pt (II), Zr, Hf
3-6 M HCl	Fe (III), Co (II), Ge, Nb*
1-3 M HCl	Zn, Ga, Mo (VI), In, Sn (IV), Te (IV), Te (VI), Au (as AuI_2^-), Pb
< 0.01 M HCl	Sn (II), Hg (II), Bi, Sb (V) slowly
3 M $HClO_4$	Po, Cd, Sb (III), Sb (V) slowly
1 M NH_4OH	Pd, Ag, Sb (III), Sb (V)
1 M NaOH	W
Not Eluted	Tc*, Ru, Th, Re, Os, Ir, Pt (IV), Au (III), Tl (III)

* In trace concentrations only.

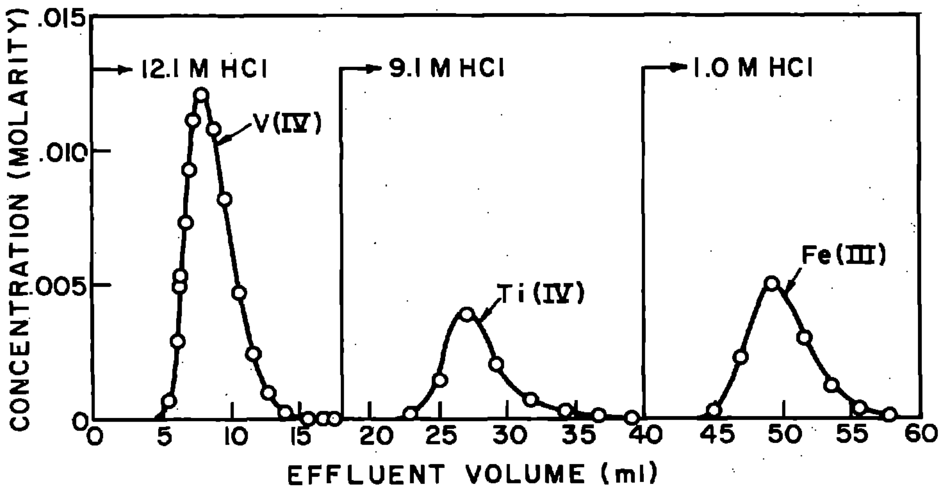


Figure 8. Separation of V(IV), Ti(IV) and Fe(III) by anion exchange (18.6 cm. x 0.49 cm^2 Dowex-1 column; 1 ml 0.05 M V(IV), 0.018 M Ti(IV), 0.025 M Fe(III) in 12 M HCl.

the case of vanadium (III), only slight adsorption is found to take place in 12 M hydrochloric acid. Vanadium (V), however, which forms an intensely brown-colored solution in concentrated hydrochloric acid, can be adsorbed strongly by an anion exchange resin, giving rise to a dark brown band. Figure 8 (124) shows the separation of vanadium (IV) from titanium (IV) and iron (III) on a column of Dowex-1 anion exchange resin. Since vanadium (IV) is only very slightly adsorbed from 12 M hydrochloric acid, it elutes first, while the titanium (IV) and iron (III) are more strongly adsorbed and hence remain on the column when eluted with concentrated hydrochloric acid. The distribution of these three ions from hydrochloric acid is shown in Figure 9 (123).

The distribution of vanadium (IV and V) between hydrofluoric acid and Dowex-1 anion exchange resin has been studied by Faris (125), along with a study of many other ions throughout the periodic table. Faris' results are shown in Figure 10; he found

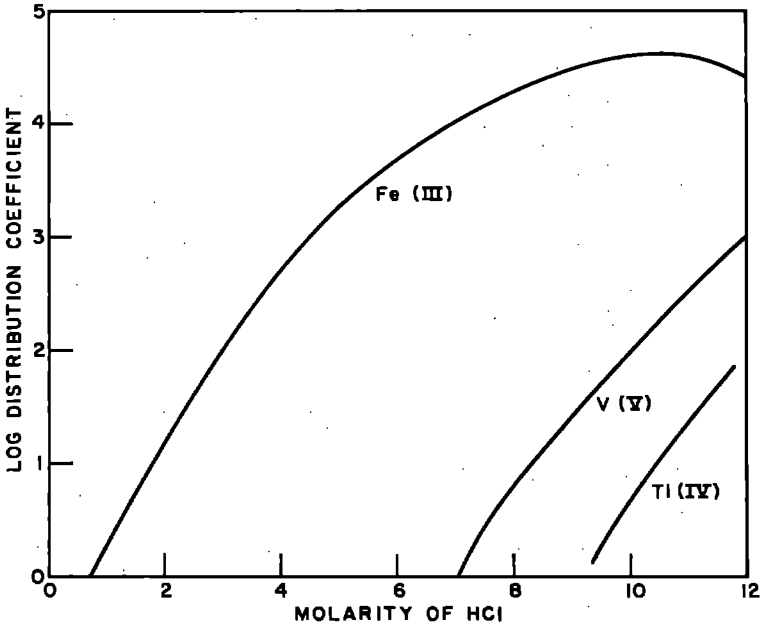


Figure 9. Distribution of Vanadium (V), Iron (III) and Titanium (IV) Between HCl Solution and Dowex-1.

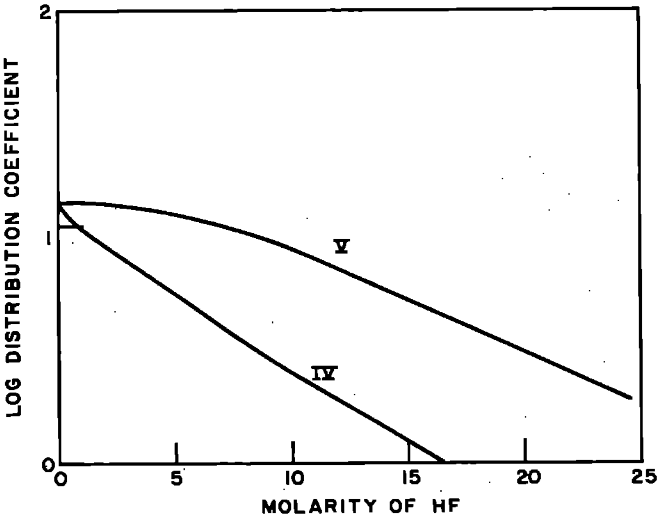


Figure 10. Distribution of Vanadium (IV and V) Between HF Solution and Dowex-1 Anion Exchange Resin.

that neither vanadium (IV) nor (V) produced a definite peak in their elution, indicating possible oxidation or reduction of these species as a result of contact with the resin.

Anion exchange resins have been employed (126) to separate vanadate from sodium and potassium ions in solution and for the quantitative estimation of the vanadate adsorbed. A mixture of these ions is passed through a column of Dowex-2 resin in the hydroxide form. Sodium and potassium are not adsorbed, of course, but the vanadate is adsorbed, displacing hydroxide ions from the resin. The amount of vanadate present in the mixture can then be determined by titrating the liberated hydroxide with standard acid.

Samuelson, Lunden and Schramm (127) have devised a useful method for the removal of several cations from solutions containing alkali salts. The method is based on the observation that a number of cations can be adsorbed on an anion exchange resin saturated with anions capable of forming strong complexes. Tartrate, citrate, and oxalate are examples of the complex-forming anions used. Cobalt (II), nickel (II), copper (II), iron (III), and vanadium (IV) are adsorbed quantitatively on an anion exchange resin in the citrate form, while the alkali metals are not. The alkali metals elute with water, leaving the above ions behind on the column. The adsorbed ions can be eluted with hydrochloric acid solution.

Molybdenum is separated from solutions containing lead, copper (II), iron (III) and vanadium (IV) in a procedure devised by Klement (128). Molybdic acid, as the citrate complex, passes through a column of sulfonic acid type cation exchange resin in the hydrogen form, while lead, copper (II), iron (III) and vanadium (IV) cations are strongly adsorbed. After elution of the molybdic-citrate complex and washing the column with water, the adsorbed cations are eluted by means of dilute acid. For the elution of copper and vanadium, 1:9 sulfuric acid is used. Iron is best eluted with 4 N hydrochloric acid, and lead with 1:7 nitric acid.

Solutions containing vanadate, chromate, molybdate, tungstate and phosphomolybdate cannot be adsorbed successfully by cation exchanges in the hydrogen form. A portion of these anions is retained on such resins as a result of partial transformation into cations by reduction (124) or as a result of precipitation (110). Separations of these ions from cations can be performed readily, however, on columns of cation exchanges in the ammonium form.

A few separation schemes involving ion exchange separations have been devised specifically for the isolation of radiovanadium formed during cyclotron bombardments. Schindewolf and Irvine (129) utilize the fluoride form of an anion exchange resin to adsorb titanium and scandium, while vanadium (IV) passes through (see procedure 7, Section VII). Another procedure, due to Walter (130), separates radiovanadium from tracer amounts of radioscandium and milligram amounts of titanium by passing an oxalate solution of these elements through a column of Dowex-1. No traces of radioscandium activity are found in the eluate, and titanium contamination is less than 20 micrograms per milliliter of effluent. (cf. procedure 11, Section VII).

V. PROBLEMS ASSOCIATED WITH DISSOLVING VANADIUM-CONTAINING SAMPLES

Many minerals containing vanadium are readily attacked by mineral acids, an initial treatment by hydrochloric acid followed by nitric acid usually being all the treatment necessary for complete extraction of vanadium (131). Any insoluble residues, generally devoid of vanadium, can be made soluble by fusion with sodium carbonate and dissolution of the melt in hydrochloric acid.

This solution is then added to the main body of solution. If silica is not to be determined, the solution of insoluble residue from acid treatment of a vanadium-containing sample can be accomplished by means of hydrofluoric acid, which is then eliminated by evaporation with sulfuric acid or by repeated evaporation with hydrochloric or nitric acids. The usual treatment of a gross sample with hydrofluoric acid, followed by evaporation with sulfuric acid to eliminate the HF, is not recommended since volatile fluorides or oxyfluorides of vanadium may be formed at red heat.

The materials which readily yield their vanadium content to the above treatment include vanadinite, carnotite, descloizite, cuprodescloizite, eusynchite and other naturally occurring vanadates (132), in addition to most of the common vanadium-containing alloys. Patronite may also be dissolved by this method if most of the sulfur present is first removed by ignition.

The vanadium present in roscoelite does not appear to respond to the acid treatment outlined above, possibly because of its presence in a silicate complex. Material of this sort is best treated by fusion methods. Many vanadium minerals which are not attacked appreciably by acids will yield to fusion with sodium or potassium carbonate (to which a small amount of niter is added), or sodium peroxide. Certain types are also susceptible to attack by sodium or potassium hydroxide fusion, conducted in nickel or iron crucibles, followed by dissolution of the melt in acid.

A major disadvantage of most fusion techniques lies in the rather long period of heating required for complete fusion. A very useful and short method for effecting solution of many vanadium-containing materials, including biological tissue, involves a sodium peroxide fusion in nickel or iron (requiring approximately two minutes for completion), followed by rapid cooling of the melt and crucible and subsequent dissolution of the melt in acid (133) (see also procedures 1 and 6 , section VII). Solution of finely ground geological materials encapsulated in gelatin has been found (134) to occur in the molten sodium peroxide in somewhat less than one minute. Variable amounts of nickel crucible are dissolved, but in general do not interfere with the subsequent analysis. Often, samples are encountered which fuse or otherwise react with the molten peroxide with explosive force, hence it is usually advisable to wear safety glasses and to conduct the fusion behind a safety shield of shatterproof glass or plastic.

A fairly complete review of fusion methods and reagents has been compiled by Calkins (135). In this compilation insoluble residues are classed as acid insolubles, alkaline insolubles, and refractory oxides, (acid and alkaline insolubles). Methods of dissolution for each of these classes are presented.

VI. COUNTING TECHNIQUES FOR VANADIUM ISOTOPES

While the number of radioactive nuclides of vanadium may not be as large as that found for many of the other elements, among their radiations are found most of the more common modes of decay. Beaufait and Lukens (136) have an excellent compilation of general counting procedures, as well as techniques and self-absorption curves for several nuclides other than vanadium. Coryell and Sugarman (137) have a section on counting techniques in general, but the material is not the very latest. Scintillation techniques were not widely known at the time this work was published, hence are not touched upon. P. R. Bell (138) has an excellent discussion of scintillation techniques, using beta and gamma radiations.

Using as criteria a long half-life and energetic radiations, it would appear that there are no really good vanadium isotopes suitable for use as tracers. Vanadium-48, having two relatively energetic gamma rays of high abundance, (Fig. 11), in addition to

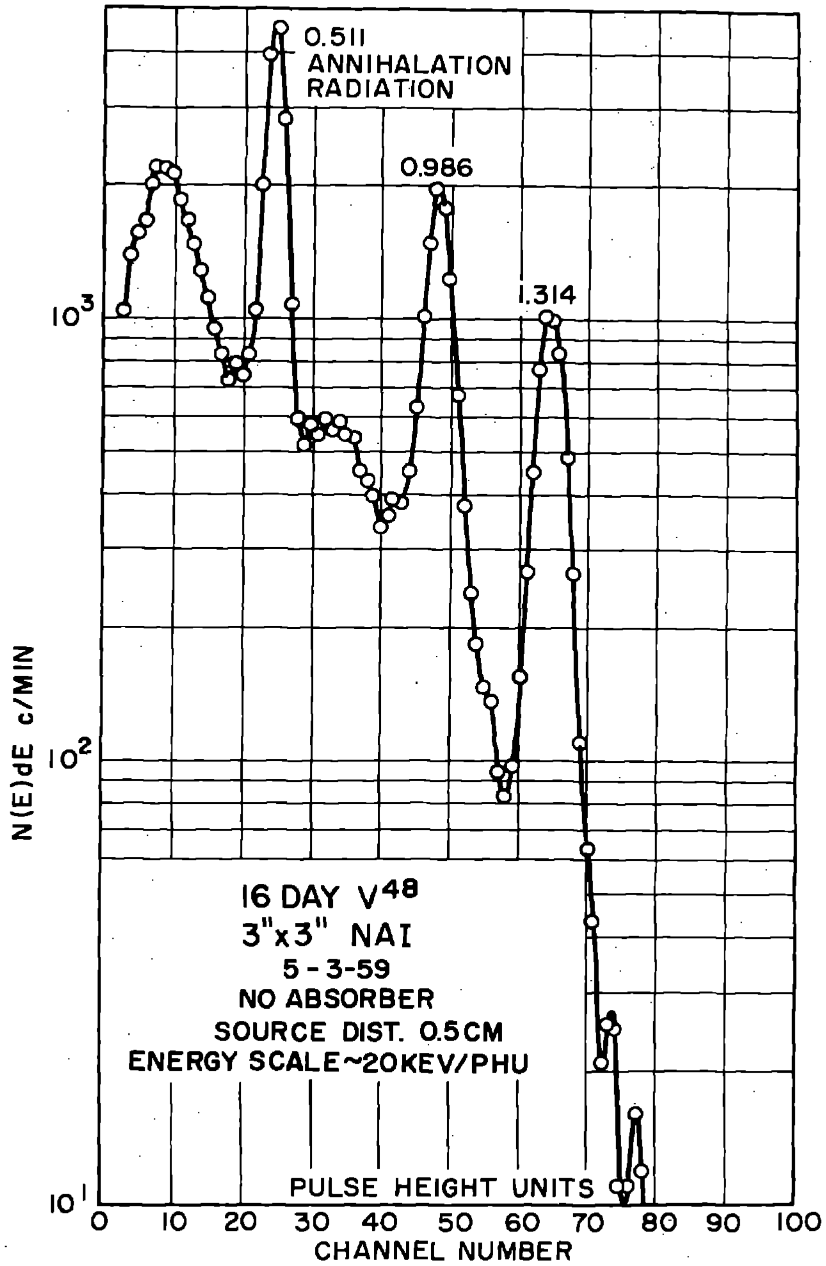


Figure 11. Gamma Spectra of Vanadium-48. The 2.30 Mev sum peak is not shown. (139)

a rather intense annihalation radiation, has been used successfully as a vanadium tracer. However, its relatively short half-life (16 days) limits its general applicability. The absolute counting efficiencies for the two most abundant gamma rays of V^{48}, 0.986 Mev and 1.314-Mev, are 18.5 percent and 17.0 percent (139) respectively at a distance of 1.0 cm from a 3" x 3" NaI(Tl) cylinder; for a standard well counter (1-1/2" diameter x 2", well 3/4" x 1-1/2" deep), these efficiencies are approximately 22 percent and 20 percent (140), respectively.

The 330-day isotope, V^{49}, has a half-life which makes it suitable for use as a tracer; however, it decays completely by electron capture, with accompanying X-radiation. Hence, in use as a tracer, V^{49} cannot be counted with very great efficiency by means of G-M or proportional type counters. One must therefore rely upon the use of scintillation or X-ray counters. Since X-rays would be expected to undergo an appreciable loss in energy in penetrating the aluminum can generally surrounding a scintillation crystal, this method would allow only moderate sensitivity, but would probably be the most practical.

The isotope formed on neutron irradiation of naturally occurring vanadium isotopes has a very short half-life, 3.74 minutes, and therefore is of no use as a tracer. It has been used in the activation analysis for vanadium by the author, however. The beta ray emitted is of sufficiently high energy (2.47-Mev) to allow use of G-M or proportional type counters. Self absorption of various vanadium-52 precipitates would not be expected to be too great upon using counters of this type. This effect would not be so apparent when a scintillation counter is used, inasmuch as the bremsstrahlung is counted with greater efficiency than in the case with G-M or proportional counters. The gamma spectrum of this isotope, (Fig. 12), is quite simple, consisting of a single gamma ray of 1.433-Mev. This gamma radiation can be counted with 16.5 percent (139) absolute efficiency by a 3" diameter x 3" NaI(Tl) scintillator at a distance of 1.0 cm, and with an efficiency of approximately 20 percent (140) in a standard well crystal.

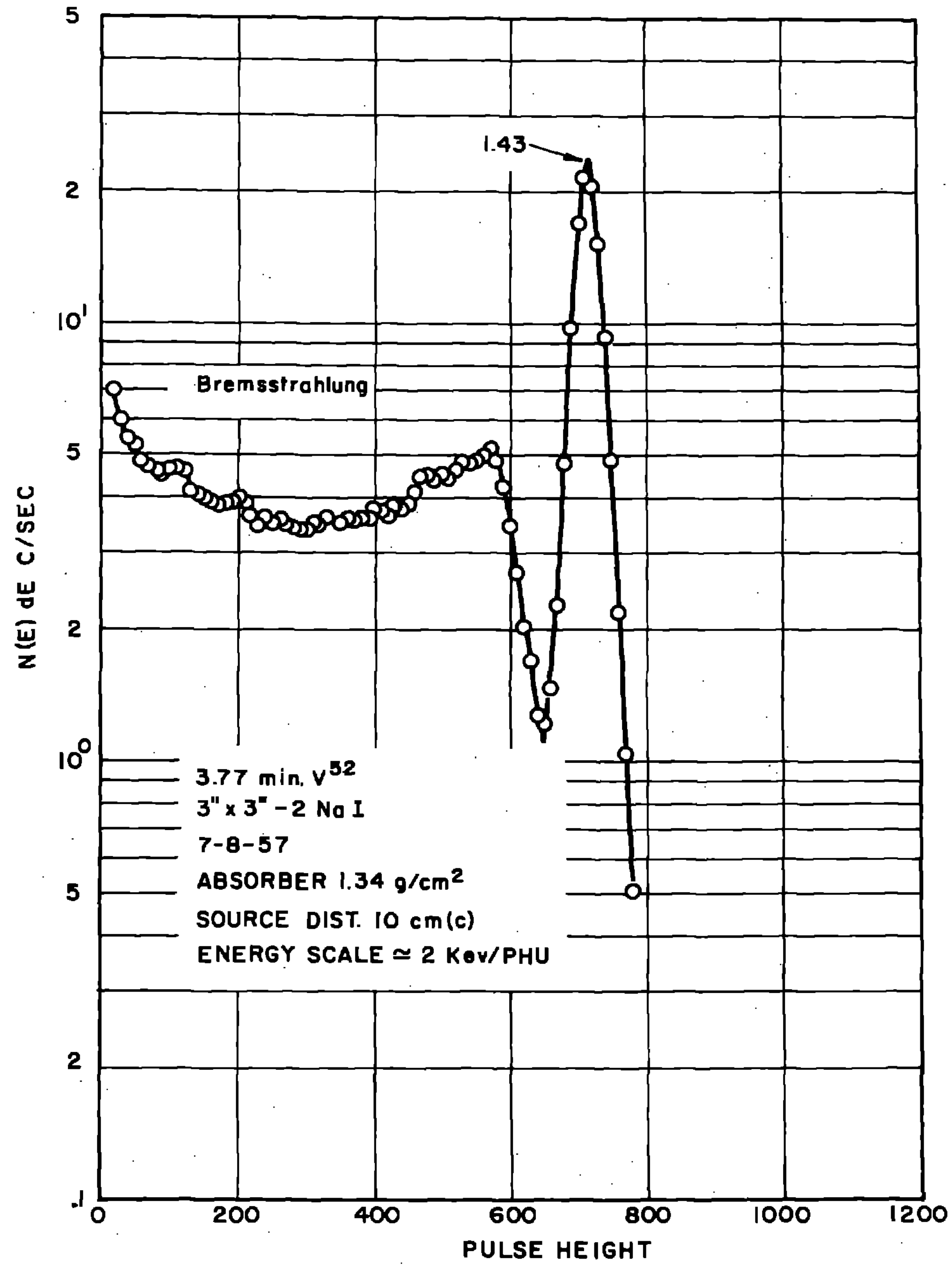


Figure 12. Gamma Spectra of Vanadium-52. (139)

VII. Collected Radiochemical Procedures

For Vanadium

PROCEDURE 1

Source: J. L. Brownlee, Jr.

Target material: Petroleum cracking catalyst (Al_2O_3 - SiO_2 base) irradiated in gelatin capsule	Time for Separation: 10 min.
	Equipment required: Standard
Type of bombardment: Neutron (fission spectrum); 10 min. at reactor power level of 1000 KW	Yield: Variable (18-70%)

Degree of purification: Sufficient for gamma spectrometry

Advantages: Complete removal of aluminum and gamma activities having energies greater than 1.4 Mev; rapid separation

Procedure

Step 1. Place a known amount of vanadium-48 activity in a 30 ml nickel crucible and evaporate to dryness. Add 3-4 gm of sodium peroxide and bring to the molten state before the sample irradiation has been completed.

Step 2. Fuse 40-100 mg finely ground sample (note 1) and gelatin capsule with sodium peroxide for two minutes (note 2). Cool crucible and contents rapidly by dipping base of crucible into cold water until the contents have solidified (note 3).

Step 3. Dissolve the solidified melt in a solution containing 16.7 ml concentrated HCl, 3 ml aluminum carrier, 0.5 ml vanadium (V) carrier, and 15 ml of 3% hydrogen peroxide, diluted to 50 ml (note 4).

Step 4. To this solution, add 30 ml of a 10% solution of 8-hydroxyquinoline in 1:4 acetic acid, followed by approximately 60 ml of concentrated ammonia (note 5). A large yellow-green precipitate of aluminum 8-hydroxyquinolinate is formed.

Step 5. Filter the precipitate through a 120-mm medium sintered glass funnel. Wash the precipitate with a minimum of dilute ammonia.

Step 6. Acidify the filtrate with HCl. Cool by adding chipped ice or liquid nitrogen directly into the filtrate (note 6).

Step 7. Transfer the filtrate to a 250 ml separatory funnel containing 5 ml chloroform previously equilibrated with 1-2 N HCl (note 7). Add 6 ml of 6% aqueous cupferron (note 8). Extract for one minute and allow 30-60 seconds for separation of the layers.

Step 8. Transfer the chloroform layer to a counting tube and analyze the gamma activity with a multi-channel gamma spectrometer.

Chemical yield: Determine with vanadium-48 tracer.

Notes:

1. Samples were hand ground or machine ground in agate before irradiation.

2. The gelatin capsule is attacked vigorously by the molten peroxide. As soon as the capsule and sample are inserted, the cover should be clamped down onto the crucible and held in place with crucible tongs until the reaction subsides. Safety glasses and a safety shield should be used during this and subsequent operations.

3. It is imperative that the contents of the crucible be solid and as cool as possible before dissolving the melt. If the melt is too hot, a violent reaction will ensue, causing radioactive contamination and resulting in possible injury.

4. The hydrogen peroxide forms a peroxy complex with vanadium and prevents reaction with the 8-hydroxyquinoline.

5. The pH of the final solution should be of the order of 9-10.

6. Vanadium cupferrate is decomposed by heat and will not extract into organic solvents, hence the temperature should be kept as low as possible.

7. If liquid nitrogen is used to cool the filtrate, care must be taken that all of the nitrogen has been evaporated off before the

separatory funnel is shaken, or the pressure created on shaking may be sufficient to break the funnel.

8. The cupferron solution should be made fresh daily and kept under refrigeration if possible.

PROCEDURE 2

Source: J. L. Brownlee, Jr.

Target material: Titanium Foil

Type of bombardment: Deuteron, ~ 7.8 Mev (Univ. of Michigan Cyclotron)

Degree of purification: Sufficient for gamma spectrometry and half-life determination

Time for separation: 4-6 hours

Equipment required: Standard

Yield: Undetermined (~ 0.1 mc)

Advantages: Apparently good decontamination - no "foreign" gamma photopeaks present in gamma spectrum of separated vanadium-48.

Procedure

Step 1. Dissolve the titanium foil target in a minimum volume of concentrated HF containing scandium and vanadium carriers. Dissolution is carried out in a polyethylene beaker.

Step 2. The solution is transferred to a Lustroid centrifuge tube and the scandium fluoride removed by centrifugation. The precipitate is washed with a small volume of dilute HF; the washings are added to the centrifugate.

Step 3. A dilute solution of sodium salicylate is added to the clear centrifugate (note 1). $Pb(VO_3)_2$ is precipitated by addition of a 10% solution of $Pb(Ac)_2$ acidified slightly with HAc (note 2).

Step 4. Filter the precipitated $Pb(VO_3)_2$, and wash with a small volume of dilute ammonium hydroxide. Dissolve the precipitate in a small volume of HCl, neutralize with dilute ammonium hydroxide, and repeat Step 3.

Step 5. Dissolve the $Pb(VO_3)_2$ precipitate in a minimum of concentrated HCl. Dilute this solution to approximately 6 N in HCl.

Step 6. Cool the solution (note 3), and add a 6 per cent aqueous solutinn of cupferron (note 4). Filter the brown-colored vanadium cupferrate and wash with a small volume of 0.05 N HCl.

Step 7. Transfer the precipitate and filter paper (note 5) to a small beaker. Add a small volume of fuming nitric acid and concentrated sulfuric acid to destroy organic matter (note 6). When the solution is clear, heat to fumes of SO_3.

Step 8. Cool the solution, and dilute cautiously 1:1 with water. Add 6 per cent aqueous cupferron (note 4).

Step 9. Filter the vanadium cupferrate and wash with 0.05 N HCl. Transfer the precipitate and filter paper to a small beaker. Add the minimum amount of fuming nitric acid to destroy the filter paper and the cupferrate.

Step 10. Allow the acid solution to cool. Dilute with deionized water to a convenient volume. Solution can be used as vanadium-48 tracer. The yield is approximately 1 μc.

Notes:

1. Sodium salicylate complexes the dissolved titanium and retards its carrying on the precipitate.

2. The solution must be kept slightly acid if the precipitation of lead hydroxide is to be prevented.

3. The solution is cooled somewhat since vanadium cupferrate is sensitive to heat.

4. The cupferron solution is best kept in a refrigerator to retard decomposition.

5. An "ashless" grade of analytical filter paper should be used for this filtration.

6. Ordinary concentrated nitric acid attacks the filter paper and precipitate more slowly - in some cases taking as long as one-half hour to decompose the organic matter. This step is best carried out in covered beakers. Safety glasses are recommended.

PROCEDURE 3

Source: Cassatt, W. A., Ph.D. Thesis, University of Michigan, Department of Chemistry, 24 September 1954

Target material: Titanium foil (2 mils thick) Time of separation: Approx. 4 hours

Type of bombardment: Deuteron (~ 7.8 Mev) Equipment required: Standard

Degree of purification: Not known Yield: Undetermined

Procedure

Step 1. Dissolve the target in a minimum volume of HF; add scandium and vanadium carriers (10 mg/ml).

Step 2. Transfer the solution to a Lustroid centrifuge tube. Remove scandium fluoride precipitate by centrifugation. Wash the precipitate with a small volume of HF; add the washings to the centrifugate.

Step 3. Make the filtrate basic with approximately 6 N NaOH to precipitate $T{:}O_2 \, . \, x \, H_2O$. Filter; make the filtrate 6 N in HCl.

Step 4. Add a 6 percent aqueous solution of cupferron to precipitate with dilute HCl. Transfer the precipitate to a beaker, and destroy the organic material by adding fuming nitric acid. Add a small volume of acetic acid to the clear solution.

Step 5. Neutralize the above solution with ammonium hydroxide. Add a solution of $Pb(Ac)_2$ to precipitate $Pb(VO_3)_2$. Wash the precipitate with dilute ammonium hydroxide.

Step 6. Dissolve the $Pb(VO_3)_2$ in the minimum volume of concentrated HCl. Add scandium and titanium carriers (10 mg/ml). Repeat steps 4 and 5 twice more.

Step 7. Precipitate purified vanadium as $Pb(VO_3)_2$. Filter onto a 15 mm filter disc. Mount the precipitate and count.

Remarks:

The decay of the beta-ray activity was followed by counting the beta particles emitted in the region of 1.35 Mev with a beta-ray spectrometer. Analysis of the decay curve obtained showed the presence of a 35± 3-minute activity, and a four-hour activity. Gamma photons emitted by the sample were analyzed with a gamma-ray scintillation counter, and the resulting curves resolved. These data indicated a 30 ± 3-minute activity and a 3.5 ± 0.5-hour activity. Gamma-ray energies, determined with a gamma scintillation spectrometer, were found at 0.329, 0.422, 0.515, 0.588, 0.682, 0.795, and 0.897 Mev with a precision of 5%. It was estimated that the 0.588 Mev line decayed with a half-life between 20 and 40 minutes, and that the other lines decayed with a half-life between 3 and 5 hours.

PROCEDURE 4

Source: Fukai, R., in AECU - 3887

Target material: Biological ash (Seaweed and marine life)

Time for Separation: ~4 min.

Type of bombardment: Neutron (in pneumatic tube) 10 min. at reactor power level of 100 KW

Equipment required: Standard

Yield: 41.5% ± 1%

Degree of purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure

Step 1. Irradiated ash is digested for 30 sec. in 15 ml. of hot 4 M NaOH solution containing 10 mg-V-carrier.

Step 2. Add 10 ml of conc. HCl to dissolve the ash. Dilute the solution to 50 ml with water.

Step 3. Transfer the solution to a separatory funnel in which 10 ml of chloroform is already placed.

Step 4. Add 2.5 ml of 6% cupferron aqueous solution and shake vigorously for 30 sec.

Step 5. Let stand for 40-60 sec. to separate the layers.

Step 6. Transfer the organic layer to marked tubes and count. (See remarks.)

Remarks

In this case both the scintillation well counter (1" x 1-1/2" NaI(Tl) crystal) and 100-channel γ-spectrometer (3" x 3" NaI(Tl) crystal) were used for counting. Two 5 ml counting samples were used, one for each counter.

PROCEDURE 5

Source: Fukai, R., in AECU - 3887

Target material: Biological ash (seaweed and marine life)

Type of bombardment: Neutron (in pneumatic tube) 10 min. at reactor power level of 100 kw.

Time for Separation: ~10 min.

Equipment required: Standard

Yield: ~30%

Degree of purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure

Step 1. Place the irradiated ash in a beaker containing 15 ml of hot 4 M NaOH solution and 10 mg Vanadium (V)-carrier. Heat 30 sec. on a burner to digest the ash.

Step 2. Add 5-6 ml of concentrated HCl to dissolve the ash. Heat for a while if necessary.

Step 3. Add 3 drops of 10% $SnCl_2$ solution to reduce V^{5+} to V^{4+} (blue solution should be obtained).

Step 4. Dilute the solution to approximately 50 ml with distilled water.

Step 5. Adjust pH of the solution to approximately 5 by using 1 M NaOH solution and testing with Hydrion pH-paper. (Faint grey-white precipitate of tin should appear.)

Step 6. Transfer the contents of the beaker to a separatory funnel. Add approximately 50 ml of 0.25 M TTA-benzene solution and shake vigorously for 30 sec. (Green color appears in organic layer).

Step 7. Add 25 ml of 6 M HCl to the separated organic layer and shake 30 sec. to recover V^{4+} in inorganic layer.

Step 8. Add 5-10 drops of 1 M $KMnO_4$ solution to oxidize V^4 to V^5 .

Step 9. Add 2 ml of 6 percent aqueous cupferron solution while cooling in a dry ice bath. Allow to stand for approximately 1 minute to allow the precipitate to settle.

Step 10. Filter onto 1-inch paper. Mount the precipitate for counting.

Remarks:

Chemical yield determined with vanadium-48 tracer or standardized vanadium carrier.

PROCEDURE 6

Source: Kaiser, D., in AECU - 4438

Target material: Biological tissue (Wet rat liver and kidney)

Type of bombardment: Neutron (in pneumatic tube) 10 min. at reactor power level of 1 megawatt

Time for Separation: ~5 min.

Equipment required: Standard

Yield: 40-45%

Degree of purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure

Step 1. Irradiate sample 10 min. at 1 Megawatt (approximately 10^{12} n-cm^{-2}-sec^{-1}).

Step 2. Fuse sample in 10 gms Na_2O_2 containing vanadium-48 tracer, 10 mg of vanadium carrier, and 10 mg of copper holdback carrier.

Step 3. Dissolve the melt in 50 ml water, and add 42 ml concentrated HCl.

Step 4. Add 10 gms of tartaric acid, bubble in H_2S gas, and filter.

Step 5. Add 10 ml 6% aqueous Cupferron solution to vanadium filtrate, and extract with 10 ml $CHCl_3$.

Step 6. Collect organic layer, and count with 100-channel analyzer.

Remarks: Chemical Yield: Determined by means of tracer vanadium-48.

PROCEDURE 7

Source: Schindewolf, U. and Irvine, J. W.,
Anal. Chem. 30, 906 (1958)

Target material: Titanium foil

Time for Separation: ~1-1 1/2 hrs.

Type of bombardment: Deuteron

Equipment required: Standard plus polystyrene ion exchange columns.

Yield: > 90%

Degree of purification: Decontamination factor for Sc and Ti $> 5 \times 10^3$

Advantages: Carrier-free vanadium-48 tracer.

Procedure

Step 1. Dissolve bombarded titanium foil in few ml concentrated HF in high temperature polyethylene test tube. Heat on steam bath if necessary.

Step 2. Add few drops of H_2O_2. Evaporate to dryness.

Step 3. Dissolve material in 0.5-2.5 M HF. Saturate with SO_2 gas.

Step 4. Pass solution through anion exchange column in the fluoride form (obtain fluoride form by equilibration of resin with 0.5-2.5 M HF). Elute vanadium with 5-10 column volumes of 0.5-2.5 M HF in polystyrene column.

Remarks: For absorption of 1 gm titanium use polystyrene column 1.3 cm in diameter x 25 cm long.

PROCEDURE 8

Source: Lemmerman, R. D., Irving, NP-1797, July 1950, pp. 54-5

Target material: Chromium metal or Cr_2O_3

Time for Separation: ~2-3 hrs.

Equipment required: Standard

Type of bombardment: Deuteron

Yield: ~90%

Degree of purification: Very good

Advantages: Procedure short; radiochemical purity of carrier-free V^{48} good. Mn^{52} can be separated from aqueous phase following V extraction.

Procedure

Step 1. Dissolve chromium metal target in hydrochloric acid. If target is chromic oxide, fuse with sodium hydroxide and sodium peroxide, cool, and dissolve melt in hydrochloric acid. (CAUTION!! Safety glasses and shield should be used!!)

Step 2. Make HCl solution 1 f. in potassium thiocyanate, 10^{-2} f. in 8-hydroxyquinoline.

Step 3. Adjust the pH to ~ 2.0 with potassium hydroxide.

Step 4. Extract several times with methyl isobutyl ketone pre-equilibrated with a solution 1 f. in KSCN and at pH 2.0.

Step 5. Combine methyl isobutyl ketone layers; wash repeatedly with 1 f. KSCN to reduce contamination of Mn^{52}.

Step 6. The solvent can be removed by careful evaporation and the residue taken up in dilute acid.

Remarks: Mn^{52} can be isolated from the aqueous phase remaining after extraction of V^{48} in ~ 95% yield.

PROCEDURE 9

Source: Batzel (From W. W. Meinke, AECD 2738, 30 Aug. '49, p. 29)

Target Material: Copper foil (~1 gm)

Time for Separation: Approx. 2 hrs.

Type of bombardment: 184-inch cyclotron (all particles)

Equipment required: Standard

Yield: Fair; Undetermined

Degree of Purification: Undetermined (only probable impurities are Cr and P)

Procedure

Step 1. Dissolve the target in a minimum amount of concentrated HNO_3; add carriers Zn through Cl, boil off HNO_3, and make 1 N in HCl.

Step 2. Add H_2S, centrifuge off the copper. Wash copper with 1 N HCl and resaturate with H_2S. Add wash to supernate.

Step 3. Boil down to 6 ml to remove H_2S, add concentrated HNO_3 and boil down almost to dryness, and make volume to 5 ml with concentrated HNO_3; cautiously add $KClO_3$ and boil for one minute.

Step 4. Centrifuge off the MnO_2. Wash MnO_2 with 6 N HNO_3, and add wash to the supernate.

Step 5. Boil down to remove HNO_3 and HCl, and make 1 N in HNO_3. Cool to 5-10°C and add an equal volume of diethyl ether. Add 5 drops of 30% H_2O_2 and immediately stir vigorously to extract chromium. Draw off the ether layer, and wash water layer with one-half volume of ether, stirring vigorously to extract any chromium left. Draw off the ether layer and add to the original ether layer.

Step 6. Almost neutralize the water layer with NaOH and pour into 10 ml of a hot solution of 1 N NaOH. (A small amount of Fe^{+++} must be present.) Centrifuge off hydroxides of Ni, Co, Fe, Ti, Sc, and Ca. Wash the precipitate with 4 ml of hot 1 N NaOH. Add wash to supernate.

Step 7. Scavenge by adding one drop of Fe^{+++} carrier (10 mg/ml) and 500 λ Ti^{+4} (10 mg/ml) to the hot solution. Centrifuge and wash the precipitate with 4 ml of hot 1 N NaOH.

Step 8. Boil down to 6 ml. Make slightly acid with acetic acid and add 5 ml of 10% $Pb(Ac)_2$. Centrifuge off $Pb(VO_3)_2$, and wash with slightly acidic, dilute $Pb(Ac)_2$. Add wash to supernate (containing Zn^{++}).

Step 9. Make 2 N with HNO_3, precipitate Pb as the sulfide by adding H_2S. Centrifuge and wash the precipitate with 2 N HNO_3. Add wash to supernate. Boil to remove H_2S.

Step 10. Neutralize with NaOH, make slightly acid with HAc and reprecipitate vanadium as lead vanadate. Weigh.

Remarks:

Reference: Scotts Standard Methods of Chemical Analysis, p. 1036.

PROCEDURE 10

Source: Haymond, Maxwell, Garrison and Hamilton (UCRL-473)

Target material: Titanium (ca. 1 gm)

Type of bombardment: 60" D_2

Degree of purification: At least factor of 10^3.

Time for Separation: 4-5 hrs.

Equipment required: Standard

Yield: 80-95%

Advantages: Carrier free. Suitable for use in biological systems

Procedure

Step 1. Dissolve the Ti powder target material in a minimum volume of 36 N H_2SO_4 and evaporate to dryness.

Step 2. Add 5.0 gm of Na_2CO_3 and 0.1 gm $NaNO_3$ and fuse the mixture at 500°C for 30 minutes.

Step 3. Extract the carrier free vanadium (presumably as vanadate) from the insoluble titanium oxide by repeated washings with cold water.

To remove any Ca or Sc activities which may have extracted with the V:

Step 4. Acidify the solution with HCl, add 10 mg of Ca and Sc, and ppt from 1 M Na_2SO_3.

Step 5. Neutralize the solution containing V with 12 N HCl and evaporate to dryness.

Step 6. Separate the V activity from most of the NaCl by extraction with approximately 5 ml of 12 N HCl.

Step 7. Evaporate the HCl solution to dryness and dilute with water to give an isotonic saline solution of V which can be used in biological studies.

Remarks:

The target consisted of C.P. metal powder supported on a copper target plate 0.25 mil Ta foil. The target was "cooled" for 24 hours after bombardment.

PROCEDURE 11

Source: R. I. Walter (J. Inorg.
Nucl. Chem., 6, 63 (1958)

Target material: Titanium

Type of bombardment: Deuteron

Yield: ~80% $V^{48,49}$

Degree of purification: Excellent

Advantages: Carrier-free $V^{48,49}$

Time for Separation: ~2-3 hrs.

Equipment required: Standard, plus ion-exchange column and apparatus in Fig. I.

Procedure

Step 1. Titanium foil target placed folded into V-shape to fit into furnace (see Figure 13). Sweep system with helium. Heat to 400°C.

Step 2. Cool trap I with ice, trap II with dry ice. Pass through chlorine gas until target completely converted to $TiCl_4$. Cool furnace.

Step 3. Warm trap II to room temperature. Sweep system with helium.

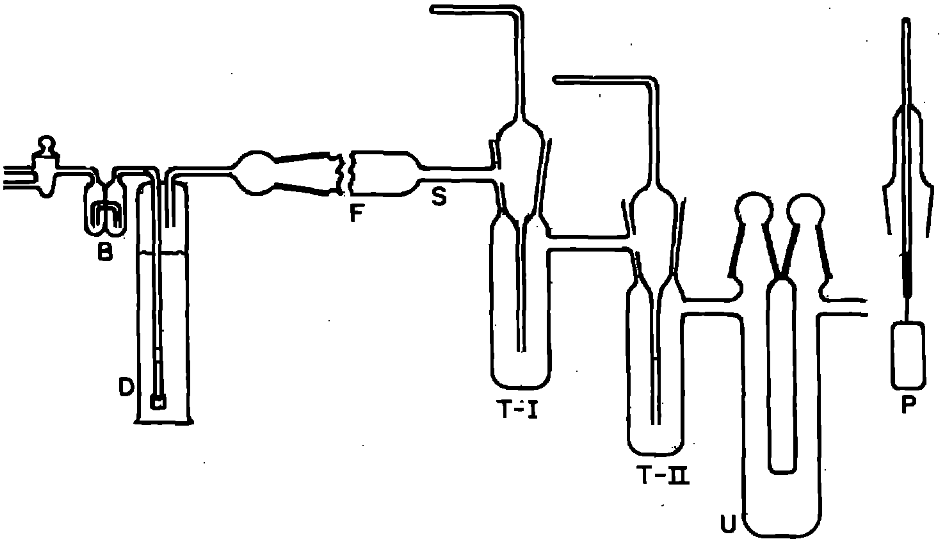


Figure 13. Apparatus for the preparation and distillation of $TiCl_4$, and for the separation of dissolved vanadium from the distillate. Helium or hydrogen gas is admitted through the stopcock, bubbler B, and drying tower D. Vycor furnace tube F is connected through a graded seal S to the Pyrex trap system. Traps T-I and T-II are made from 6 mm right-angle vacuum stopcocks. The U-tube is filled with glass wool, and connected to a drying tube. All horizontal connections beyond S should slope downward to facilitate drainage of $TiCl_4$. Copper paddle P is mounted as shown on a 24/40 joint which can replace the stopcock plug of either trap, and simultaneously seals the inlet to it.

Step 4. Close inlet to trap I. Distill $TiCl_4$ into trap II.

Step 5. Prepare copper paddle (P) by heating to dull redness, immersing in methanol and drying. Insert into trap II in place of stopcock.

Step 6. Reflux $TiCl_4$ for ~ 30 minutes. Cool; rinse paddle in CCl_4. Immerse in 1 M HCl.

Step 7. Saturate 1 M HCl solution with H_2S, filter, wash and evaporate filtrate just to dryness.

Step 8. Dissolve dry residue in 0.1 M oxalic acid. Saturate with SO_2 gas.

Step 9. Charge solution to 1 x 15 cm ion-exchange column with Dowex-1. Follow with second column of Dowex-1 0.5 x 5 cm. Elute with 0.1 M oxalic acid. Destroy oxalic acid in product solution with H_2O_2.

Note: Moisture should be excluded from the system as far as possible, since VCl_4 is decomposed by water.

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