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RADIOCHEMISTRY

OF TITANIUM

NUCLEAR SCIENCE SERIES

COMMITTEE ON NUCLEAR SCIENCE

Radiochemistry of Titanium

by Vincent J. Landis

San Diego State University
San Diego, California

and

James H. Kaye

Battelle—Northwest
Richland, Washington

Revised Edition

Subcommittee on Radiochemistry
National Academy of Sciences-National Research Council

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 radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

Contents

Contents (Continued)

Radiochemistry of Titanium

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San Diego State University
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Battelle—Northwest
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I. General Reviews of the Inorganic and Analytical Chemistry of Titanium

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1

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II. General Reviews of the Radiochemistry of Titanium

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National Nuclear Energy Series, Vol. 1, Div. VIII, (McGraw Hill
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III. Isotopes of Titanium

Table I (see page 4) is a list of the isotopes of titanium.

IV. The Inorganic Chemistry of Titanium

A. General Chemistry

Excellent and current reviews of the general chemistry of titanium are
listed in the "General Reviews" section. Although titanium is one of the most
abundant and ubiquitous elements, it has traditionally been treated as a rare ele-
ment because of the difficulty of reducing the ores. It has been found in almost
all crystalline rocks, sands, and soils, as well as in vegatation, natural waters,
meteorites, stars, and deep sea dredgings[3]. Titanium is estimated to constitute
0.6 percent of the lithosphere, making it the ninth most abundant element and the
fourth most plentiful structural metal[4]. Ferrotitanium, titanium dioxide and
titanium tetrachloride have been widely used for many years, but the metal has
been produced on a commercial scale only since 1948[3,5]. Table II shows some
properties of titanium of interest to the chemist.

3

TABLE I

Table of Isotopes of Titanium (2)*

Isotope	Natural Abundance, %	Atomic Mass (C^{12} Scale)	Half Life	Mode of Decay	Energy of Radiation, MeV	Thermal Neutron σ, barns
Ti^{41}		40.9841	.090s	β^+		
Ti^{42}		41.973	.25s	(β^+ & E.C.)	6.0	*
Ti^{43}		42.9707	0.56-0.58s	β^+	β^+ 5.8	
Ti^{44}		43.96234	46-48yr	E.C.	γ_1 0.068 (90%) γ_2 0.078 (98%)	
Ti^{45}		44.960998	3.05-3.10h	β^+, E.C.	β^+ 1.04	
Ti^{46}	7.95-7.99	45.955887				0.60
Ti^{47}	7.75-7.32	46.955073				1.7
Ti^{48}	73.45-73.99	47.951517				8.0
Ti^{49}	5.51-5.46	48.951442				1.9
Ti^{50}	5.34-5.25	49.948569				0.14
Ti^{51}		50.95026	5.79-5.80m	β^-	β^- 2.14 γ 0.320 (95%) 0.605 (1.5%) 0.928 (15%)	

*All data from reference (2) except Titanium 42
data from reference (144).

FIGURE I

Chart of the Nuclides in the Titanium Region. Reference 1.

						Mn 50 0+ 2m 0.29s β+ β+6.6 γ.66- 1.45 E7.6	Mn 51 45m β+2.2 γ.74,1.17 E3.2	Mn 52 6+ 2lm 5.7d β+2.63 ε,β+.58 IT.38 γ1.43, γ1.43 .94,.74, E4.71	Mn 53 7/- ~10⁶y ε noγ E.60	Mn 54 3+ 3l4d ε γ.84 E1.38	Mn 55 5/- 100 σ13.3 55.9381	Mn 56 3+ 2.58h β−2.66,1.05,.75, γ.84,1.81,2.11,·· E3.71	Mn 57 1.7m β−2.6,1.1 γ1.22,.914,.137, .22−.71 E2.7
Mn 54.9380 σ 13.3													
Cr 51996 σ 3.1			Cr46 1.1s β+	?Cr47 0.4s β+	Cr 48 23h ε γ.30,.12 E1.4	Cr 49 42m β+1.54,1.39,.73 γ.09,.06,.15 E2.56	Cr 50 4.31 σ 17.0 49.9461	Cr 51 7/- 27.8d ε γ.32 E.75	Cr 52 83.76 σ.8 51.9405	Cr 53 3/- 9.55 σ18 52.9407	Cr 54 2.38 σ.38 53.9389	Cr 55 3/- 3.5m β−2.5 noγ E2.5	Cr 56 5.9m β−1.5 γ.063,.026 E1.6
V 50.942 σ 4.9			V 45 ~1s β+	V 46 0.42s β+6.05 E7.1	V 47 32m β+1.94, ε γ1.54,1.87 E2.96	V 48 16.1d β+.70, ε γ.99,1.31,2.25 E4.02	V 49 7/- 330d ε noγ E.61	V 50 6+ 0.24 ~6×10¹⁵y β−,ε γ.71,1.59 σ<150 49.9472	V 51 7/- 99.76 σ4.9 50.9440	V 52 3.77m β−2.7 γ1.43 E4.0	V 53 2.0m β−2.53 γ1.01,·· E3.54	V 54 55s β−3.3 γ.99,.84,2.21	
Ti 47.90 σ 6.1			Ti 43 0.4s β+5.6 E6.6	Ti 44 ε(β+[47]) γ.079,.070, (1.16,··) E.155,	Ti 45 7/- 3.08h β+1.02 ε γ E2.06	Ti 46 7.93 σ.6 45.95263	Ti 47 5/- 7.28 σ1.7 46.9518	Ti 48 73.94 σ8.0 47.94795	Ti 49 7/- 5.51 σ1.9 48.94787	Ti 50 5.34 σ.14 49.9448	Ti 51 7/- 5.80 β−2.13,1.52 γ.32,.93,.61 E2.46		
Sc 44.956 σ 23		Sc 40 0.18s β+9.2 γ3.75 E14	Sc 41 7/- 0.55s β+5.61 E6.6	Sc 42 62s 0.66s β+2.82 β+5.53 γ1.52, 1.23,44 E7.13 E6.55	Sc 43 7/- 3.9h β+1.19,.82 γ.37 E2.22	Sc 44 2+ 2.4d 4.0h IT.27 β+1.47,ε γ1.16, .58−27 E3.65	Sc 45 7/- 100 σ(10+13) 44.95592	Sc 46 4+ 20s 84d IT.14 β−.36,·· ε γ1.12,.89; σ.25 E2.37	Sc 47 3.4d β−.44,.60 γ.16 E.60	Sc 48 6+ 44h β−.65,.48 γ1.31,1.04,.99, .17 E3.99	Sc 49 57.5m β−2.01,·· γ1.76 E2.01	Sc 50 0.35s 1.8m IT.26 β−3.6 γ.52,1.56, 1.12 E6.3	
Ca 40.08 σ.43	Ca 38 0.7s γ3.5	Ca 39 3+ 0.9s β+5.5 noγ E6.5	Ca 40 96.97 ε σ.2 39.96259	Ca 41 7/- 7.7×10⁴y ε σ40 E.41	Ca 42 0.64 σ40 41.95863	Ca 43 7/- 0.145 σ.7 42.95878	Ca 44 2.06 σ.7 43.95549	Ca 45 165d β−.25 noγ E.25	Ca 46 0.0033 σ.3 45.9537	Ca 47 4.7d β−.67,1.98 γ1.31,·· E1.98	Ca 48 0.18 σ1.1 47.9523	Ca 49 8.8m β−2.0,1.0 γ3.10,4.05,4.7 E5.2	
K 39.102 σ 2.1	K 37 3/+ 1.2s β+5.1 E6.1	K 38 0+ 0.95s 7.7m β+5.1 β+2.7 γ2.2 E6.1 E5.9	K 39 3/+ 93.10 σ2.2 38.96371	K 40 4- 0.0118 1.3×10⁹y β−1.32,ε γ1.46 σ70 E−1.32 ε+1.51 40.96184	K 41 3/+ 6.88 σ1.1 E3.53	K 42 2- 12.4h β−3.53,2.01 γ1.52,·· E1.82	K 43 3/+ 22h β−.83,.48−1.82 γ.37,.61,.22−1.00 E6.1	K 44 22m β−4.91,·· γ1.16,2.1,.48−5.0	K 45 20m β− γ.18,1.7,··		K 47 18s β−4.1,3.5,·· γ2.0,2.6	

NOTES: This chart may be obtained from Battelle Northwest Laboratories, Richland, Washington 99352.
The General Electric Chart of the Nuclides (to December 1968) is available from Educational
Relations, The General Electric Company, Schenectady, New York.
The Karlsruhe Chart (1968) may be obtained from Gersbach and Sohn Verlag, München 34,
Barer Strasse 32, Germany.

FIGURE II

Decay Schemes of Titanium Radioisotopes (2)
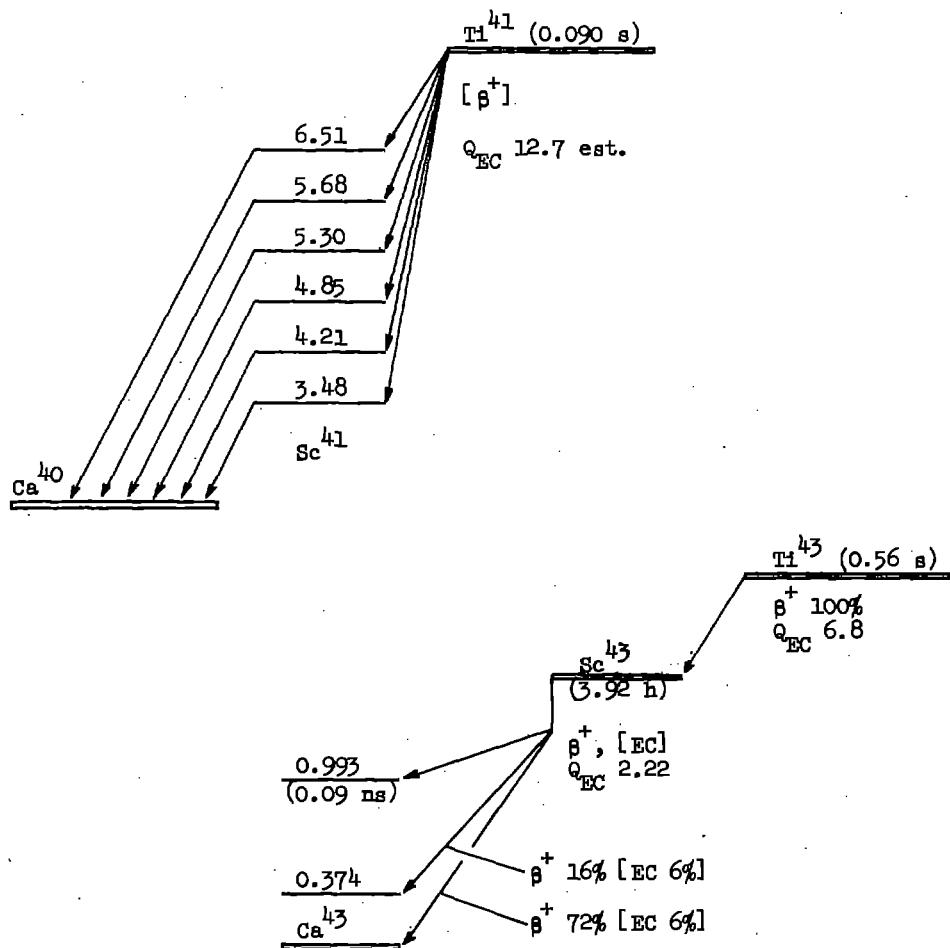
(Continued)

FIGURE II (Continued)

Ti^{44} (48 yr)

EC (Q_{EC} 0.16)

0.1463
(0.15 μs)
0.0678

Sc^{44}
(3.92 h)

0.9%

2.66

2.28

1.88

1.156

β$^+$ 94%
EC 5%

Ca^{44}

Ti^{45} (3.09 h)

0.09%

0.27%

0.05%

Q_{EC} 2.059 calc.

EC + β$^+$ 0.39%

β$^+$ 84% [EC 15%]

1.663

1.408

1.238

0.718

Sc^{45}

Ti^{51} (5.8 m)

β$^-$

Q_{β^-} 2.46

6%

0.930

94%

0.3198
(0.2 ns)

V^{51}

7
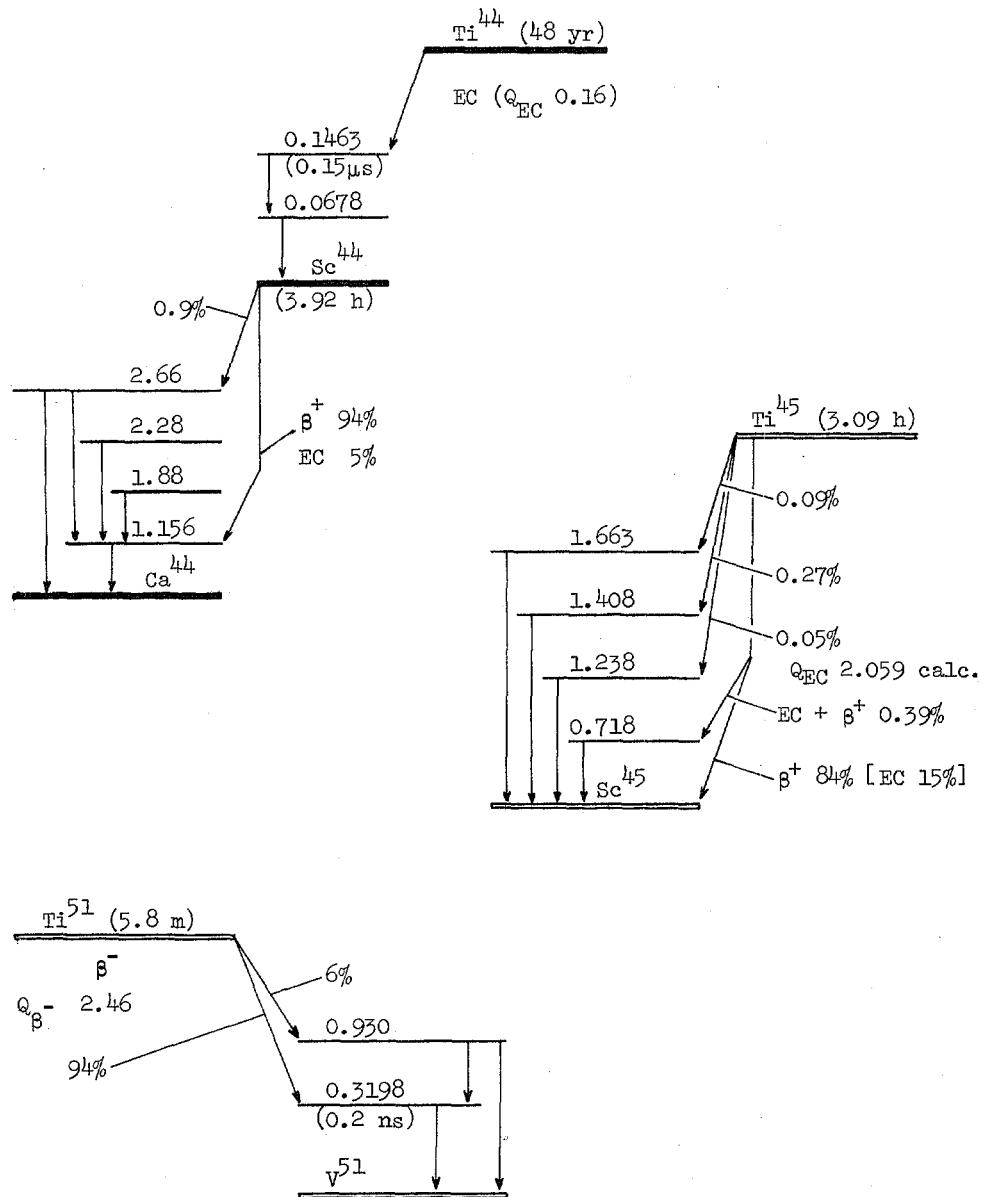
TABLE II

Properties of Titanium

		Reference
Density	4.54 g/cc	3
Melting Point	1668°C	3
Boiling Point	3260°C	3
Electron Ground State	[Ar] $3d^2\ 4s^2$	4
Oxidation States	4+ Most stable	4
	3+ Stable in water; oxid by air	4
	2+ Oxid by air/water; useful in fused salts	4
	0 Metal or Ti(dipy)$_3$ only	4
	-1 Ti(dipy)$_3$ only	4
Ionic Radius	0.68 Å (+4)	6
Covalent Radius	1.32 Å	6
Ionization Potential		
1st	6.83 e.v.	6
2nd	13.57 e.v.	6
3rd	28.14 e.v.	6
4th	48.24 e.v.	7

Oxidation Potentials:

$$Ti^{\circ} = Ti^{2+} + 2\ e^{-} \qquad E^{\circ} = ca.\ 1.63\ V.$$

$$Ti^{\circ} + H_2O = TiO^{2+} + 2H^{+} + 4\ e^{-} \qquad E^{\circ} = ca.\ 0.88\ V.$$

$$Ti^{\circ} + 2\ H_2O = TiO_2 \cdot XH_2O + 4H^{+} + 4\ e^{-} \qquad E^{\circ} = 1.69\ V.$$

$$Ti^{\circ} + 6\ F^{-} = TiF_6^{2-} + 4e^{-} \qquad E^{\circ} = 1.19\ V.$$

$$Ti^{2+} = Ti^{3+} + e^{-} \qquad E^{\circ} = ca.\ 0.37\ V.$$

$$Ti^{3+} + H_2O = TiO^{2+} + 2H^{+} \qquad E^{\circ} = ca.\ -0.1\ V.$$

1. TITANIUM METAL AND ALLOYS

Most commercial production of titanium is based upon formation of the volatile tetrachloride by chlorination of the ore and subsequent reduction of the vapor with

molten magnesium[3]. The reduction of titanium tetrachloride by sodium is used
to a lesser extent. High purity titanium has been produced by the iodide refine-
ment process of van Arkel and ßeBoer for many years on a laboratory scale[8]. A
recent development in refining titanium is the electrolysis of titanium(II) or
titanium(III) salts in a fused alkali halide solution. Table III shows the rela-
tive purity of titanium metal as produced or refined by these processes. Further
purification of iodide metal as indicated by lower stress values has been
reported[9]. Typical alloying constituents for industrial titanium are 4-8%
aluminum together with lesser percentages of vanadium, zirconium, molybdenum,
and/or chromium.

As a first approximation, titanium metal is very similar to zirconium or
stainless steel in appearance and in physical and chemical properties. At room
temperature, massive titanium is resistant to all common gases, salts, alkalies,
mineral acids (except HF) and most liquid metals[10]. Hydrofluoric acid and
fluorboric acids react vigorously with titanium metal, even when hot nitric acid
forms an oxide film on titanium and fails to dissolve the metal. Refluxing with
1:1 HCℓ in the absence of air will dissolve chips of titanium in 8 to 10 hours
forming a purple titanium(III) solution, but in the presence of air some dioxide
precipitates. Similar treatment with dilute sulfuric acid dissolves some of the
metal but also forms a blue-gray bulky precipitate which covers and protects the
remaining metal.

At elevated temperature, titanium will burn in many gases. Reaction takes
place at 150°C in fluorine[12], 350°C in chlorine, 360°C in bromine, 400°C in
iodine, 610°C in oxygen, 800°C in nitrogen, 700 to 800°C in steam and 1200°C in
air[13]. Heating in an open flame causes a blue film to form on the surface of
a piece of metal. Techniques for dissolution of titanium metal and alloys are
given later.

2. OXIDES OF TITANIUM

There are three well-defined oxides of titanium, TiO, Ti_2O_3, and TiO_2,
which correspond to the positive oxidation states of titanium[14]. The first

9

TABLE III

Typical Analyses of Titanium Metal

	Mg Reduced Commercial Percent [3]	Iodide Refined Percent [3]	Electrolytic Percent [11]
Iron	0.2-0.03	0.025-0.0035	<0.005
Chromium			<0.005
Magnesium	0.12-0.04	0.002-0.0015	0.002
Sodium			
Silicon	<0.01	<0.03	0.01
Manganese	0.06-0.03	0.013-0.005	0.03
Copper	<0.03	0.002-0.0015	<0.006
Aluminum	<0.005	0.05-0.013	<0.04
Nitrogen	0.05-0.01	0.004-0.001	0.002
Hydrogen			0.008
Oxygen	0.15-0.005	0.01-0.005	0.002-0.025
Carbon	0.03-0.01	0.03-0.01	0.08
Vanadium			<0.005
Chlorine			0.10
Molybdenum		0.0015	
Nickel		0.003	
Tin	<0.03	<0.01	

two are readily subject to oxidation to the extremely stable dioxide. Titanium(II) reduces water but titanium(III) and titanium(IV) are readily precipitated as hydrous oxides from aqueous solutions. The purple titanium(III) hydrous oxide precipitated by base from water is a very strong reducing agent. Titanium(IV) hydrous oxide is stable and may be ignited to the dioxide. Freshly precipitated hydrous dioxide can be dissolved in strong acid or alkali but the product of

10

aging, ignition, or precipitation from hot solutions requires hot concentrated sulfuric acid, preferably containing ammonium sulfate, or alkali fusion, to effect speedy solution[6].

Several solid peroxytitanium(IV) compounds of somewhat uncertain composition and structure are often included in the group of "titanium oxides"[15]. Peroxytitanium(IV) species are of great importance to the solution chemistry of titanium. Their color is the basis for the common spectrophotometric method of analysis, they are used to prevent hydrolysis, and can serve as a "holdback" to prevent precipitation[16]. In the presence of peroxide, titanium(IV) can be dissolved in strong alkali[17], but reprecipitates upon decomposition of the peroxide.

3. OXIDATION STATES OF TITANIUM

As can be deduced from Table II, the radiochemist is likely to be concerned only with titanium metal and with titanium(IV) compounds. Oxidation potentials alone do not reflect the titanium redox picture completely for several reasons. Titanium(IV) and, to a lesser extent, titanium(III) require several molar acid or, alternatively, complex-forming reagents to prevent hydrolysis. As a result, the exact species or the ionic strength is in sufficient doubt to cause significant possibility for error in the measured potentials.

Anhydrous titanium(II) may be purchased as the hydride, halide or oxide and methods for analysis have been devised[14]. These compounds react with water to form hydrogen and titanium(III). Aqueous titanium(III) solutions must be protected from air or even mild oxidizing agents. Titanium(III) salts and solutions of the chloride can be obtained commercially. Titanium(III) sulfate in acid solution slowly produces noticeable amounts of H_2S and titanium(III) is one of the very few ions known to reduce perchlorate in aqueous solution[18]. The common volumetric analysis for titanium is based upon the reduction of acidic titanium(IV) solutions by cadmium or zinc amalgam, or by aluminum metal, followed by titration of the resulting titanium(III) with a standard oxidizing agent[14]. Since titanium, unlike iron, is not reduced by a silver-silver chloride reductor.

11

titanium and iron can be co-determinated by redox methods[19]. Solutions of titanium(III) are used to some extent as reducing agents both in analysis and in kinetic studies. References to the preparation and uses of such solutions are given in the Meites "Handbook of Analytical Chemistry[20].

4. SOLUTION CHEMISTRY OF TITANIUM(IV)

A. Simple Aqueous Solutions

Extreme susceptibility to hydrolysis requires that solutions of titanium(IV) salts in non-complexing media be maintained at high acidity with low titanium concentration. The ionic species of titanium(IV) in such aqueous solutions has long been designated as TiO^{2+} because evidence for either a hydrated tetrapositive ion or hydrolytic polymers has been lacking[7]. The predominate truly hydrolytic species in nitric and perchloric acid solutions has been the subject of considerable study[21-26].

Liberti, Chiantella and Corgliano[26], the most recent authors, have studied the partition of titanium(IV) between aqueous solution and 8-hydroxyquinoline in chloroform and TTA in benzene. They propose the following species and equilibrium constants:

$$*K \equiv [Ti(OH)_2{}^{2+}] [H^+] / [TiOH^{3+}] \qquad pK = 1.80$$

$$K \equiv [Ti(OH)_3{}^+] [H^+]^2 / [TiOH^{3+}] \qquad pK = 4.20$$

$$K \equiv [Ti(OH)_4] [H^+]^3 / [TiOH^{3+}] \qquad pK = 6.3$$

Their data indicate the following formulation of the solubility product.

$$Ksp \equiv [TiOH^{3+}] [OH^-]^3 \qquad pK = 39.4$$

Nabivanets[22] reported the following solubility products.

$$Ksp \equiv [TiO^{2+}] [OH^-]^2 \qquad pK = 29$$

$$Ksp \equiv [TiO(OH)^+] [OH^-] \qquad pK = 16.5$$

Nabivanets' sets of values do not disagree greatly with the constants for similar expressions derived from Liberti's results. The apparent disagreement con-

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*To avoid possibility of ambiguity read "K ≡" as "the equilibrium constant expression defined as ... "

cerns which species exist in moderately acid solutions. These results stress further the practical necessity of using approximately one molar solutions of nitric or perchloric acid to prevent hydrolytic precipitation in solutions of titanium at room temperature. About 5 M acid concentration is required to prevent precipitation in such solutions upon boiling.

Polarographic reversibility and changes in half-wave potential, as well as changes in hydrolysis characteristics, indicate that weak complexes are formed by titanium(IV) in hydrochloric, sulfuric, and phosphoric acid solutions[27]. Such complexes retard hydrolysis somewhat, but it is advisable to use the above acidities as a guide for the preparation of stable carrier solutions in most acids.

"Aging" effects of titanium solutions were studied by Babko[21]. His results confirmed the previous indications[23] that, unlike zirconium, titanium(IV) does not form short-chain polymeric species by hydrolysis. All "aging" effects, such as slow ion-exchange adsorption and a slow color reaction with hydrogen peroxide, were found to coincide with the Tyndall effect indicating colloidal aggregations.

B. Hydrochloric Acid Solutions

In electromigration studies of hydrochloric acid solutions of titanium(IV) Nabivanets[22] has found that a dispositive species predominates from pH 1.3 to 4 M HCl, a neutral species ($TiOCl_2$) predominates from 4M to 10M, and an anionic predominates in greater than 10M HCl. The latter finding confirms the results of ion exchange studies by Kraus[28].

C. Sulfuric Acid Solutions

Several indications are available that sulfuric acid solutions of titanium(IV) contain sulfate and/or bisulfate complexes, and that these complexes are stronger than the chloride species. Nabivanets[22] obtained the following equilibrium constants.

$$K_1 \equiv [TiO^{2+}] [SO_4^{2-}] / [TiOSO_4], \qquad pK = 2.40 \text{ at } 18°C$$

$$K_2 \equiv [TiOSO_4] [SO_4^{2-}] / [TiO(SO_4)_2^{2-}] \qquad pK = 1.20 \text{ at } 18°C$$

13

The work of Beukenkamp and Herrington[23], on the other hand, was interpreted to indicate bisulfate complexation in sulfuric acid solutions and the following constants were derived.

$$K_1 \equiv [Ti(OH)_2^{2+}] / [Ti(OH)_3^{+}] [H^{+}] \qquad K_1 = 2.0$$

$$K_2 \equiv [Ti(OH)_3 HSO_4] / [Ti(OH)_3^{+}] [HSO_4^{-}] \qquad K_2 = 11 \text{ to } 12$$

$$K_3 \equiv [Ti(OH)_2 HSO_4^{+}] / [Ti(OH)_2^{2+}] [HSO_4^{-}] \qquad K_3 = 0.64$$

There is general agreement that a neutral complex predominates at a sulfuric acid concentration of about 0.5 molar, but in more acidic solutions a neutral species is indicated by Beukemkamp and a negative species by Nabivanets.

5. INORGANIC SALTS

A. Soluble Compounds

As discussed in the previous section, there are really no water-soluble simple salts of titanium. Titanium(III), much like iron(III), must be maintained at low pH, and titanium(IV) solutions require an acid concentration of several molar to prevent hydrolytic "aging" or precipitation. On the other hand, most simple salts, other than ignited dioxide, are readily soluble in acid solution, or in the presence of a complexing agent such as citrate or tartrate. Solubilities recorded for some commercially available complex salts at room temperature are: Na_2TiF_6 – 65 g/ℓ, $(NH_4)_2TiF_6$ – 250 g/ℓ, and K_2TiF_6 – 12 g/ℓ[29]. However Ginsberg[29] reported hydrolysis difficulties in conjunction with these studies. Almost any titanium compound or mineral can be dissolved in either hydrofluoric-sulfuric acid mixtures or by fusion in ammonium or potassium bisulfate.

B. Insoluble Compounds

From the standpoint of quantitative or semiquantitative precipitation, the most commonly utilized insoluble inorganic compound of titanium is the hydrated dioxide. Other precipitants include the acid phosphate[17], arsenate[30], ferrocyanide[5,14], ferricyanide[14], and potassium iodate[5]. The hydrous oxide tends to be very gelatinous and to occlude other substances, so a good deal of effort has gone into the development of methods for producing a more crystalline

14

and pure product. Alkali hydroxide causes non-quantitative precipitation due to amphoterism (in very strong base) or the formation of colloidal suspensions. The addition of iron(III), zirconium, or other carrying agent is helpful. Procedures for carefully adjusting the pH have been described using ammonia[17], pyridine[31], barium carbonate[16,17], thiosulfate[16,17], acetic acid[14,16,32], hexamethylamine[31], guanidine carbonate[5,33], and benzoic acid[14]. Precipitation by boiling in acid solution is an effective preliminary separation from many elements and is a classical method for separation from aluminum, chromium, etc.[17]. Zirconium, phosphate, and complexing reagents interfere.

Under most of the conditions above, a fairly gelatinous hydrous oxide or basic salt is formed. It is probably safe, therefore, to assume that titanium(IV) would serve as a carrier for most other transition metal ions and vice versa. The most similar reagent to titanium(IV) under most circumstances is zirconium(IV).

Duval[34] has reported on thermogravimetric studies of titanium dioxide formed with various reagents. The following temperatures are necessary for ignition of these precipitates to stoichiometric TiO_2: aqueous ammonia (350°), guanidinium carbonate (550°C), tannin (600°C), selenite (880°C), peroxide and oxalate (320°C), cupferron (643°C), 8-hydroxyquinoline (718°C), 5,7-dibromooxine (480°C). Several of the organic titanium compounds have a definite composition at a lower temperature and are discussed under the topics "Chelates" or "Methods of Determination."

C. Volatile Titanium Compounds

The volatile tetrachloride of titanium has traditionally found application as a purification method for titanium and has been used in radiochemical separation of titanium from other transition metals[35]. The tetrachloride is prepared commercially by chlorination of titanium ores. On a laboratory scale it may be prepared by heating TiO_2 with carbon black, and then reacting with chlorine at 550°C or above[36,37]. Other methods involve heating TiO_2 with CCl_4, $CHCl_3$, phosgene, or CO and Cl_2[38]. The tetrachloride is a light yellow liquid, with a melting point of -30°C, a boiling point of 136.4°C, and a density

of 1.726. Chlorides with lower boiling points include: $SiCl_4$ (57°C), $SnCl_4$ (113°C), $AsCl_3$ (122°C), $GeCl_4$ (84°C). Volatile chlorides with higher boiling points include VCl_4 (164°C), $NbCl_5$ (243°C), $TaCl_5$ (234°C), $FeCl_3$ (319°C). Copper wool may be added before distillation to react with vanadium.

6. COMPLEXES OF TITANIUM

Consideration in this section is given only to titanium(IV) complexes which are formed in, or extractable from, aqueous media. For one who wishes to study air-oxidizable titanium(III) complexes, and the extremely hydrolysis-sensitive titanium(IV) complexes, starting sources may be found in reviews and articles by Jorgensen[39], Shiihara[40], and Rivest[41,42]. Most of the known constants are given in the Chemical Society's Special Publication #17[39].

Complexes of both titanium(III) and (IV) are substitution labile and their chemistry is free from the disadvantages, and occasional advantages, associated with inert complexes such as those of chromium(III) and cobalt(III)[44]. Because titanium(IV) has not been found as a simple hexaaquo-ion, it may be considered to always exist in aqueous solution as oxo-, hydroxo-, or other complexed species. Titanium(IV) exhibits a strong "preference" for oxygen as a donor atom with fluoride as the only monodentate challenger. Most strong chelating ligands for titanium have at least one oxygen donor atom, but nitrogen or sulfur can form the second bond without losing effectiveness.

A. Monodentate Ligands

Hydrogen Peroxide

The yellow to orange color formed by titanium solutions upon addition of hydrogen peroxide is the most common means of detection and determination of titanium. This complex is not strong enough to forestall hydrolysis so quantitative interpretation of the results is difficult. From considerable solid and solution studies, Patel and Jere[45] concluded that the peroxide anion usually acts as a bidentate ligand. Uninhibited by the facts, we have chosen to follow the conventional wisdom by including this discussion with simple complexes rather than chelates.

16

Patel and Jere[45] have studied the titanium(IV)-peroxide system in perchloric and sulfuric acid solutions, and also in the presence of chelating ligands. The summary of their results below shows the dependence of the titanium(IV)-peroxide equilibrium upon other coordinated groups.

$$K \equiv [TiOX] \, [H_2O_2] \, / \, [TiXO_2]$$

$$X = \text{oxalate,} \quad pK = 6.10$$

$$X = \text{maleate,} \quad pK = 4.72$$

$$X = \text{malonate,} \quad pK = 4.55$$

$$X = \text{sulfate,} \quad pK = 4.19 \text{ (in 0.75 M } H_2SO_4\text{)}$$

Without committing himself as to the exact species involved, Babko[46] calculated the following equilibrium constant for the ions in which the Ti(IV):peroxide ratio is 1:1.

$$K \equiv [Ti(IV)] \, [H_2O_2] \, / \, [Ti(IV)H_2O_2] \qquad pK = 3.05 \text{ (in HCl)}$$

Mori[47] and co-workers studied the titanium(IV)-hydrogen peroxide system in aqueous sulfuric acid and concluded that the species below were appropriate.

pH 0 to 2 $[Ti(OH)_2(H_2O)(H_2O_2)]^{2+}$ or $[TiO_2]^{2+}_{aq}$

pH 3 to 6 $[Ti(OH)_3(H_2O_2)]^+$

pH 7 to 9 $[Ti(OH)_3(HO_2)]$ or $[Ti(OH)_2O_2]$

pH 10 to 13 $[Ti(OH)_2(O_2)_2]^{2-}$
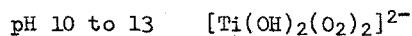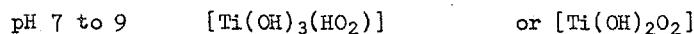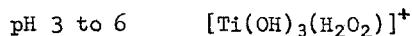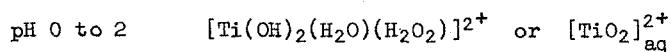
Fluoride

The fluoride complexes of titanium(III) and (IV) are widely utilized in preventing hydrolysis and in the dissolution of titanium containing metals and minerals. Kleiner[48] studied the aqueous system Ti(IV) – H_2O_2 – F^- and calculated the following constant for a 0.1 M nitric acid medium.

$$K \equiv [TiO^{2+}][F^-] \, / \, [TiOF^+] = 3.6 \times 10^{-7} \qquad pK = 6.44$$

Since K_2TiF_6 can be prepared from acidic aqueous solution, it is reasonable to assume that negative fluoride complexes are formed in solution. Cotton[4]

states that $TiOF_4^{2-}$ is the predominate species in HF solutions and that $TiOF^+$, $TiOF_2$ and $TiOF_3^-$ also exist.

Thiocyanate

The thiocyanate complex of titanium(IV) has been investigated by spectrophotometry and extraction by Delefosse[24,25] who calculated the following equilibrium constant for the complex in 1M perchloric acid.

$$K \equiv [Ti(OH)(SCN)^{2+}] / [TiOH^{3+}] [SCN^-] \quad pK = -1.7$$

She found the higher complexes to be extremely sensitive to hydrolysis. A titanium(IV) thiocyanate complex which is somewhat stable in acetone has been used to extract titanium from aqueous solution and to determine titanium(IV) spectrophotometrically[49].

Monodentate Organic Ligands

Color changes and changes in solubility indicate complex formation between titanium(IV) and a number of organic compounds which are presumed to serve as monodentate ligands. Such compounds have only one functional group or else have multiple functional groups so located that steric considerations render their serving as chelates improbable. Welcher[50] lists those used for titanium analysis up to about 1946, Sommer[51] includes several in his review of colorimetric reagents for titanium(IV). Caulfield and Robinson[52] studied the color forming reactions of titanium(IV) with 27 phenols, many of which must serve as monodentate ligands. The brief listing below is intended to give a feeling for the variety of such reagents known.

TABLE IV

Some Monodentate Color Reagents for Titanium(IV)

o-phenylphenol	1-, or 2-napthol
hydroquinone	o-aminobenzoic acid
thymol	quinoline
o-(?), m-, & p-aminophenol	resorcinol
p-hydroxybenzoic acid	p-chlorophenol

18

B. Chelate Complexes

The general rule that chelates are more stable than analogous monodentate complexes is followed by titanium(IV). This added stability is exceptionally pertinent for titanium because so few monodentate ligands prevent hydrolysis in neutral to basic solution, and few form anionic species. Analytical chemists have long investigated titanium chelates for gravimetric, colorimetric, and electrochemical detection and determination of the element. In general, greater stability is found with chelating reagents having oxygen donor atoms separated by two or three carbon atoms such that a 5 or 6 membered ring may be formed in complex formation. The second oxygen may often be replaced by a nitrogen or sulfur atom without greatly diminishing the stability. Some such reagents are quite sensitive for titanium(IV) but none seem to have a high degree of selectivity.

Citrate, oxalate, tartrate, salicylate, lactate, ascorbate, and ethylene-diaminetetraacetate are examples of readily available materials which are used to prevent hydrolysis, to prevent precipitation or to promote polarographic reversibility. Unlike many transition metals, Titanium(IV) does not tend to combine well with beta-diketones[51].

Cupferron, 8-hydroxyquinoline and its derivatives, and tannin are among the chelating reagents commonly utilized for gravimetric determination of titanium. A very large number of other organic precipitants are known which probably chelate with titanium(IV) but which have not been as widely studied.

The unending search for spectrophotometric reagents with a high degree of sensitivity and selectivity has led to the study of a very large number of chelate-forming reagents which develop a color or change color in the presence of titanium(IV). Tiron (disodium 1,2-dihydroxybenzene-3, 5-sulfonate) and chromotropic acid (1,8-dihydroxynaphthalene-3, 6-disulfonic acid) are common examples of the o-diphenol and peri-diphenol classes of colorimetric reagent for titanium. Both of these reagents contain sulfonic acid groups to increase solubility, and both are capable of chelate complex formation with titanium(IV) in acidic solution. The latter characteristic decreases the number of inter-

19

fering cations. The stability and sensitivity of the color-forming complexing
reagents generally follows the order peri-diphenols, > o-diphenols,
> o-phenolcarboxylic acids, > o-dienols[53]. In Sommer's survey paper[51]
and Welcher's[50] treatise one may find 75 to 100 color-forming chelate
reagents.

Oxalate

The oxalate complexes of titanium(IV) may be used to prevent hydrolytic
precipitation at pH's greater than 5.0[54]. This allows the separation of
aluminum from titanium by 8-hydroxyquinoline, and aids in the separation of
titanium from niobium and tantalum[55]. The electrochemical reversibility of
the titanium(III)-(IV) couple is improved in oxalate containing solutions[56].
Pecsok[57] showed polarographically that the monooxalato complexes of titanium(III)
and titanium(IV) were of similar stability.

Babko[54] used spectrophotometry and electromigration to study the
titanium(IV) oxalate complexes and calculated the constants below.

$$K_1 = [TiO^{2+}] [C_2O_4^{2-}] \ / \ [TiOC_2O_4] \qquad\qquad pK\ 6.60$$
$$K_2 = [TiOC_2O_4] [C_2O_4^{2-}] \ / \ [TiO(C_2O_4)_2^{2-}] \qquad pK\ 3.30$$

A general review of the metal oxalato complexes has been written by Krishnamurty
and Harris[58].

Ethylenediaminetetraacetic acid

Ethylenediaminetetraacetic acid is usually referred to as EDTA, but one also
finds its sodium salts designated as Versine or complexone[III]. The most useful
property of the titanium(IV) - EDTA system is that the complex formed is not as
strong as that of most transition metals. This property allows other metals to
be "held back" while titanium is precipitated or extracted. For example, many
metals will not precipitate from ammoniacal solution in the presence of EDTA,
but titanium(IV) will. This effect is also used in the determination of
titanium with cupferron. EDTA is used to prevent the coprecipitation of most
other metal cupferrates[59].

Cupferron

Cupferron, the ammonium salt of nitrosophenylhydroxylamine, is perhaps the most useful reagent in the separation of titanium(IV) because few cupferrates form in several molar mineral acid solution. Its use as a precipitating reagent is discussed in the section on gravimetric determinations, and its use in solvent extraction is discussed in that section.

Chromotropic Acid

Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) is one of the more carefully studied colorimetric reagents and has been used for the determination of titanium since about 1900[60]. Because it is one of the better reagents for determination of titanium(IV), and it is also a representative example of a large group of compounds, it will be discussed in some detail. The colored titanium(IV)-chromotropate complex is formed in solutions which are over 75% in sulfuric acid. The interference of a large number of metal ions is eliminated at this acidity[61]. Spectrophotometry indicates the existence of complexes with 1:1, 1:2, and 1:3 metal to ligand ratios. However, because several formulas may be used to represent the metal central ion and the chromotropic acid may lose up to four of its hydrogen ions, the unambiguous interpretation of the species involved is impossible at present. Electrophoresis indicates that positive species such as $TiRH_3^{3+}$ and/or $TiORH_3^+$ predominate in solutions more acidic than pH 0.1 and that negative species predominate if the pH is greater than 0.4[62].

The colorimetric determination was stated to be most selective at pH 2 where a complex having a titanium to ligand ratio of 1:2 predominates. If several of the common interfering ions are previously reduced with ascorbic acid, niobium constitutes the only serious metal ion interference according to Sommer[62]. Methods of determining titanium with chromotropic acid have been published by Sommer[63,64], Stener[65], and by Šaarni[66].

Ortho-Diphenols

Catechol, Tiron, protocatechuic acid, and 2,3-dihydroxynaphthalene-6-sulfonic acid represent the o-diphenol class of colorimetric reagents for titanium(IV)[67,68]. Catechol is more properly named as 1,2-dihydroxybenzene. Since it has two potentially displaceable hydrogen atoms, it may be conveniently represented as RH_2. Tiron is the disodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid and its parent acid may be represented as RH_4. Protocatechuic acid is 3,4-dihydroxybenzoic acid and may be represented as RH_3. In spite of the rather great differences in substituents to the fundamental o-diphenol grouping, the constants most characteristic of chelate bond formation vary surprisingly little[69]. The fact that charge differences due to the ionization of sulfonic acid groups is significant was demonstrated by Babko[70] who found the $Ti(RH)_2$ type of complex to be extractable into organic solvents for 1,8-dihydroxynaphthalene but not for its disulfonated derivative, chromotropic acid.

In studies similar to those discussed for chromotropic acid, Sommer considered this series of ligands[67,68]. His electrophoresis studies show that a negative species predominates at pH greater than 1.5 and 1.7 for the catechol and tiron complexes and that in both systems positive species predominate in solutions more acidic than pH 1.1. He has also used catechol together with various quaternary bases to extract Fe(III), Mo(VI), Nb(V), V(IV), U(VI) and W(VI) into chloroform as a means of colorimetric analytical determination[71].

7. PRINCIPAL METHODS OF DETERMINATION OF TITANIUM

Comprehensive collections of methods for the determination of titanium in a range of materials are given by Classen[72], Codell[73], Kodama[74], and Scheffer[14]. In addition, Bachman and Banks have written a critical review of the analytical methods for the titanium, vanadium and chromium groups[31]. These analyses include gravimetric, titrimetric, spectrophotometric, electrochemical, and spectrographic methods, each with its areas of applicability. Several of the more useful methods are given below.

A. Gravimetric Methods

Hydrous Oxide

The most simple method for the determination of titanium(IV) is to precipitate and dry the hydrous oxide. Other metals which would be coprecipitated and substances which would complex titanium must be absent. The use of an ammonium acetate-acetic acid buffer system is recommended[1,18]. The diluted neutral solution is boiled vigorously for 3 minutes, filtered, washed and dried. The ignition requires a temperature of 350°C but temperatures up to 950°C are acceptable[34].

Cupferron

Since stable solutions of titanium, in the absence of complexing agents, will usually be several molar in acid, cupferron may often be added directly as a 6% aqueous solution. The precipitate may be filtered and washed repeatedly with 1:10 hydrochloric acid. The usual analytical procedure calls for adding fresh cupferron solution slowly to a chilled titanium solution which has been made about 4N in sulfuric or hydrochloric acid[14,74]. The precipitate must be ignited to TiO_2 at over 650°C because the cupferrate formed cannot be dried to a dependable composition[34].

This simple method quantitatively precipitates not only Ti, but also Zr, Hf, V, Nb, Ta, Mo, W. Fe, Pd, Ga, Sn, Sb, Bi, and Po. Elements partially precipitated are Cu, Tl, Th, Pa, Ac and the rare earths[75]. The interference of iron may be prevented by adding SO_2. The most specific gravimetric use of cupferron seems to be the addition of a 10 to 15 fold excess of EDTA prior to precipitation, followed by adjustment to a pH of 4.5 with ammonium acetate, and then precipitation with cupferron as above[59]. This method prevents interference by Zr, V, Mo, W, Fe, Sn, Sb, Bi, As (III) or (V), borate, alkali metals, and, presumably, some of the untested congeners of these elements.

Oxime or 8-Hydroxyquinoline

This reagent is commonly used for the gravimetric determination of titanium(IV). Welcher[76] gives the following procedure:

"To 150 ml. of solution containing 0.1 g. of titanium, add 1 g. of tartaric acid and 0.5 g. of sodium acetate. Add ammonium hydroxide' until the solution is neutral to phenolphthalein and then add 1.5 ml of glacial acetic acid. Heat to 60°C, stir well, and add an excess of 2 percent alcoholic 8-hydroxyquinoline reagent. Boil the mixture for 10 minutes, filter, wash with hot water, and dry at 110°C. Weigh as $TiO(C_9H_6ON)_2$. The factor for titanium is 0.1361."

This simple procedure at pH 5-8 separates titanium from Mg, Al, Fe, Cr, Th, Zn, V, U, Mo, Nb, Ta, Zr, or Hf as well as the alkali metals and alkaline earths[14]. The more acidic end of the pH range gives better separation from other metals.

Several workers have later indicated that the 8-hydroxyquinoline compound cannot be dried to dependable composition, so the precipitate is usually either ignited to the dioxide at about 700°C or determined by a bromide-bromate titration[34].

Higher molecular weight precipitates which can be oven dried are given by 5,7-dichloro-8-hydroxyquinoline and 5,7-dibromo-8-hydroxyquinoline[34]. The method of Fresenius[77] is to heat the titanium(IV) solution, which is 0.2 N in acid, to 50°C. A one to two percent solution of the reagent in acetone is added in excess. The solution is heated to boiling for five minutes and filtered while hot. After washing with 25 percent acetone containing 0.04 N mineral acid, and then with hot water, the precipitate is dried to constant weight at 150°C.

Para-hydroxyphenylarsonic Acid

The use of the sodium salt of p-hydroxyphenylarsonic acid to precipitate titanium was developed by Simpson and Chandlee[78] and has been rated as the most specific gravimetric reagent for titanium(IV)[72]. The usual procedure is to precipitate 20 to 100 mg of titanium from 100 ml of solution which is 0.9 to 2.5 N in HCl or H_2SO_4. One gram of NH_4SCN is added to hold back iron(III), and sodium p-hydroxyphenylarsonate (4 to 10 percent) is added. The mixture is boiled 15 minutes, filtered, and washed with 0.25 M HCl containing 0.5 percent

p-hydroxyphenylarsonic acid and, if iron is present, 2 percent ammonium thiocyanate. A final wash with 2 percent ammonium nitrate yields a precipitate which is ignited to TiO_2 because the original precipitate does not have a dependable composition and cannot be dried to anhydrous titanium phenylarsonate[34]. Cerium(IV), zirconium, thorium, tin(IV), and hydrogen peroxide interfere. Zirconium may be used as a non-isotopic carrier, or it may be removed by a preliminary precipitation from a 2.5 to 3.0 N HCl solution containing hydrogen peroxide. Several other arsonic acids are also fairly specific for group IV tetravalent cations, but they are better suited for separation of zirconium, tin, or thorium than titanium.

B. Titrimetric Determinations

A very common method of titanium analysis depends on the stoichiometric oxidation of titanium(III) to titanium(IV). A cadmium or zinc amalgam (Jones) reductor or aluminum metal may be used to reduce acidic titanium(IV) containing solutions. Because the resulting titanium(III) is rapidly air oxidized, the reduced solution must be either maintained in an inert atmosphere, or oxidized immediately upon formation. Standardized cerium(IV), permanganate, dichromate, iron(III) and other common oxidizing agents will quantitatively oxidize the titanium(III).

We have found it convenient to receive the titanium(III) directly into aliquots of standardized cerium(IV) sulfate solution. These solutions are stable and the excess cerium(IV) can be titrated at leisure with iron(II) ammonium sulfate solution to a ferroin (Iron(II)-(III) phenanthroline) endpoint; receiving the titanium(III) in iron(III) solution and then titrating the iron(II) formed with permanganate has also been recommended[72,74].

Another convenient method of reducing titanium(IV) is given by Scheffer[14]. A solution containing sulfuric and hydrochloric acids to a total of 5 M is put into an erlenmeyer flask. For 75 to 100 mg of titanium(IV), one gram of aluminum foil is added. A glass tube is run from the stopper of the flask to a beaker of saturated sodium bicarbonate solution. In this way air is excluded and, upon cooling, the bicarbonate siphons into the acid, furnishing a carbon dioxide

25

atmosphere. After the aluminum dissolves, the solution is boiled 3 to 5 minutes
and cooled. Two milliliters of 25% ammonium thiocyanate in water is added as
an indicator, and the titanium(III) is titrated with standard iron(III) ammonium
sulfate solution. Metals which are reduced by aluminum and reoxidized by
iron(III) interfere. These include vanadium, niobium, antimony, and chromium.

C. Spectrophotometric Methods

Hydrogen Peroxide

The yellow color formed with hydrogen peroxide is the basis of the classical
method for determining titanium. A solution containing 0.1 to 5 mg of titanium
is made about 3 N in hydrochloric or sulfuric acid and 0.3 to 0.45 percent in
hydrogen peroxide. The absorbance at 420 mμ is then compared with that of
standard solutions treated in a similar manner.

Scheffer[14] specifically recommends fusion of paper, rubber, oxides, or
siliceous minerals with 8 g. of sodium carbonate in a platinum crucible. The
resulting cake is dissolved in 40 ml. of water and 70 ml. of concentrated
hydrochloric acid. The product is evaporated to 75 ml., filtered if necessary,
and transferred to a 100 ml. volumetric flask. The addition of 15 ml. of 3%
hydrogen peroxide, mixing, and dilution to volume complete the preparation for
spectrophotometric measurement.

He recommends making standards by dissolving 0.100 g. of N.B.S. titanium
dioxide in 8 g. of ammonium sulfate and 20 ml. of concentrated sulfuric acid.
He recommends adding 90 ml. of water, filtering into a 200 ml. volumetric flask,
cooling, and diluting. Aliquots of this solution make the standards when trans-
ferred to 100 ml. volumetric flasks to which 20 ml. of 1:1 sulfuric acid and
15 ml. of 3% hydrogen peroxide are added before dilution and measurement at
420 mμ.

Phosphate may be added to prevent interference of the color of iron(III).
Many other colored ions also tend to interfere and fluoride forms a strong
complex with titanium(IV) and thereby bleaches the desired color.

8-Hydroxyquinoline and EDTA

The 8-hydroxyquinolate provides one of the most specific spectrophotometric methods for the determination of titanium(IV). Taylor[79] found that only copper and uranium interfere if titanium(IV) is extracted twice at pH 8 to 9 from 100 ml. of 0.001 M EDTA solution into 10 ml. of 1% 8-hydroxyquinoline in chloroform, and the adsorbance is measured at 400 mμ. A more detailed procedure may also be found in Morrison and Freiser[80].

Tiron, chromotropic acid, thymol, sulfosalicylic acid, and many other reagents which form colors with titanium(IV) are used in other spectrophotometric methods. Details of these methods may be found in the Fresenius handbook[72], Sandell's book[61], and other sources. The method involving ether extraction of a thiocyanate complex is discussed in the solvent extraction section.

8. SEPARATION METHODS

Most of the procedures for gravimetric analysis are, of course, also procedures for separation of titanium from other elements. In addition, solvent extraction, ion exchange, distillation, and electrolysis are each applicable to separations of titanium from other elements. There have not been very many studies of radiochemical separations of titanium, but a great deal of work has been done by analytical chemists because of the ubiquitous nature of titanium compounds.

A. Precipitation separations:

In the classical hydrogen sulfide scheme for qualitative analysis, titanium(IV) will precipitate as the hydroxide in the ammonium sulfide group of elements. It is often useful, however, to add 1% tartaric acid prior to making the solution basic, thus preventing the precipitation of titanium(IV) with this group of elements. The latter modification serves to separate iron and many of the other transition elements from the titanium(IV). If this procedure is followed by a cupferron precipitation, titanium and zirconium are recovered quantitatively with thorium, cerium and rare earth contamination[16].

27

The detailed procedures and interferences for the quantitative separations of titanium with cupferron, 8-hydroxyquinoline derivatives, and p-hydroxyphenylarsonic acid have been discussed as gravimetric determinations. A summary of precipitation separations as presented by Classen[72] is shown in Table V. For the details of any of these methods, one is referred to the original work.

B. Solvent Extraction Separations

The solvent extraction of titanium has been investigated primarily as an analytical tool. The fact that titanium is not an important fission product, and the fact that suitable isotopes have not been available for comprehensive extraction studies until relatively recently, have contributed to a lack of study by radiochemists. However, several systems of interest have been studied.

Fluoride-Ether

Titanium(IV) is extracted less than 0.05% from 1 M to 20 M HF into an equal volume of ethyl ether.[81] The failure of titanium to extract may be useful in the separation of titanium from Nb(V), Ta(V), and Re(VII) which are over 60% extracted from 20 M HF. Sn(II), Sn(IV), As(III), As(V), Ge(IV), P(V), Se(IV), V(III), V(V), Mo(VI), and Sb(III) are extracted from 5% to 40%.

Chloride-TBP or Ether

Titanium(IV) does not appear to be extracted by ether or other oxygen containing solvents from acidic chloride media. Under proper conditions Sb(V), As(III), Ga(III), Ge(IV), Au(III), Fe(III), Hg(II), Mo(VI), Nb(V), Pt(V), Pa(V), Sc(III), or Tl(III) should be extractable from titanium(IV) in acidic chloride solutions. Extraction of scandium from 8 M HCl into tributyl phosphate was used to separate Sc[44] from the parent Ti[44].[82]

TABLE V
PRECIPITATION SEPARATIONS [72]

Reagents	Titanium Precipitated From																
	Fe	Al	Ni	Co	Mn	Zn	Be	Cr	Zr	Th	Cu	Sn	V	Mo	W	U	Others
Ammonia	±[1]		+	±	+	±		±[2]	±[5]		±			+		±	Ca Group, Mg
NH₄OH & sulfosalicylic		+	+	+	+	+		+[3]								+	
Pyridine			+	+	+												Ca Group, Mg
Hexamethylenetetramine			+	+	+	±											
Chloride & bromate		+	+	+		+	+	+									Ca Group, Mg
Guanidine carbonate		+						+[2]						+	+	+	
Cupferron	±[1]	+	+	+	+	+	+	+								+	Ca, Mg, Ce
p-Hydroxyphenylarsonate	+	+	+	+	+[4]	+	+	+[3]	+[5]	+	+		+	+		+	Ca, Mg, Ce, Tl
Tannin & acetic acid		+	+	+		+										+	
Tannin & antipyridine	+	+	+	+	+	+		+									
Tannin & oxalic acid		+					+	+	+	+			+			+	
5,7-Dibromo-8-OH-quinoline		+	+	+	+	+	+	+								+	Ca, Mg
Sodium hydroxide		+				+	+	+[2]				+	+	+	+	±	

Reagents	Precipitated From Titanium																
	Fe	Al	Ni	Co	Mn	Zn	Be	Cr	Zr	Th	Cu	Sn	V	Mo	W	U	Others
H₂S, NH₃ & Citrate or Tartrate	+		+	+	±	+					+						
Electrolysis (into Hg)	+		+	+	±	+		+			+	+		+			
Na₂CO₃ fusion		+						+				+	+	+	+		SiO_2, PO_4^{3-}

+   Satisfactory separation.
±   Separation incomplete or only under special conditions.
1)   Only as divalent iron.
2)   Only as chromate.
3)   Both Cr(III) and Cr(VI).
4)   Both Mn(II) and Mn(VII).
5)   In Hydrogen peroxide containing solutions.

From A. Claassen, in Handbuch der Analytische Chemie, W. Fresenius and G. Jander (Eds.), Part III, Section IV b, Springer-Verlag, Berlin, 1950; reprinted by permission.

29

Thiocyanate-ether

Titanium(IV) is rather poorly extracted by thiocyanate into ether; however, this system is of interest for several reasons. Scandium is 89% extracted from a 7 M ammonium thiocyanate solution which is also 0.5 M in HCl, while titanium(IV) is only 13% extracted under the same conditions.[84] Titanium(III), on the other hand, is 84% extracted from 3 M ammonium thiocyanate, which is 0.5 M in HCl. These facts render probable a separation based upon extraction of many elements from titanium(IV) followed by a reduction of the titanium(IV) to titanium(III) and extraction of this from many of the remaining elements.

An analytically specific spectrophotometric extraction procedure[85] is to add 1 g. of citric acid, 1 ml of thioglycolic acid, and 3 g. of ammonium thiocyanate to 25 ml of titanium(IV) solution which has been made 6 M in hydrochloric acid. This is extracted with 15 ml of 0.01 M tri-n-octylphosphine oxide (TOPO) in hexane for five minutes. The organic phase containing the titanium is washed with 6 M sulfuric acid for 1 minute. For analysis, the organic phase is centrifuged and the absorbance measured. Nb, Ta, W, and Mo interfere. Large excesses of Y, Fe(III), Cu(II), Zr, Cr(VI), Co(II), Ni, Mn(II), V(V), Mn(VII) Pb, Dy, Tb, Ho, Yb, K, Be, Al, Ca, Sn(II), Cd, Mg, Si, Ba, B or, Li do not interfere with colorimetric determination. Ti, V, Nb, Ta, Mo, W. U, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Cu, and Bi are listed by Sandell as forming colored thiocyanates.[61]

8-Hydroxyquinoline-Chloroform

8-hydroxyquinoline (8-quinolinol, oxine) is one of the most studied extracting reagents for many metals. Taylor's 1954 Ph.D. thesis was devoted primarily to the extraction of behavior of Al, Ti(IV), V(V), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Mo(VI), W(VI), and U(VI) into chloroform by 8-hydroxyquinoline.[79] His

emphasis was upon evolving analytical methods rather than separation
per se. His principal contribution to titanium chemistry was the
previously described colorimetric determination using EDTA to hold
back other metals. Under his conditions, titanium(IV) was over 95%
extracted in the pH range of 8-9 while Mo(VI), W(VI), and V(V) were
not extracted at all above pH 8.2.

Stary,[86] in 1963, published the results of a more exhaustive
study of 8-hydroxyquinoline extractions into chloroform. He used
oxalic acid, tartaric acid, nitrilotriacetic acid (NTA), and 1,2-
diaminocyclohexanetetraacetic acid (DCTA), in addition to ethylene-
diaminetetraacetic acid (EDTA) as competing complexing agents.
Appropriate equilibrium constants were derived when possible. The
results of this work are summarized in Table VI. We have listed the
pH at which 50% of the metal is extracted at 20°C by equal volumes
of 0.1 M oxine in chloroform. Except where noted otherwise the pH
vs percent extracted curve is a steep, fairly symmetrical "S" shape
which goes from 0% extracted to 100% extracted in about 2 pH units.
The results for titanium(IV) are shown in more detail in figure III.

Quaternary Ammonium Salts--Hydrocarbons

Although quaternary ammonium salts may be found useful in the extraction
of several elements from titanium, they do not appear to be useful in the
extraction of titanium from aqueous solution. Maeck[87] reviewed extractions
by quaternary ammonium salts from 1-5 M sodium hydroxide, nitric acid,
sulfuric acid, hydrofluoric acid and hydrochloric acid solutions. No extrac-
tion of titanium or its neighbors was found, except that of vanadium(V) from
dilute hydrofluoric acid.

Tetraphenylarsonium Chloride-Chloroform

Sommer[88] found that polyphenol complexes of titanium(IV), such as
discussed under chelates, were quantitatively extracted into chloroform by

Table VI

Extraction of Metals into Chloroform by 8-Hydroxyquinoline
pH at which the extraction coefficient is unity

Z	Ion	0.10 M Oxine	0.010 M Oxalic	0.010 M Tartaric	0.010 M NTA	0.010 M EDTA	0.010 M DCTA
4	Be(II) a	5.81	7.0	6.3	7.0	8.5	8.9
12	Mg(II)	8.57 b	8.1 c	7.8 c	---	[No Extraction]	
13	Al(III)	2.87 c	6.9 c	5.6 c	8.1 ac	9.7 c	10 c
20	Ca(II)	10.38	ppt.	9.5 c	---	[No Extraction]	
21	Sc(III)	3.57	7.1	6.3	10.8 ab	10.8 ab	11.4 ab
22	Ti(IV)	1.45	2.8 a	1.5	1.9 ab	7.0 ab	8.0 ab
23	V(V)	0.88	poor	extr.	poor	poor	extr.
24	Cr(III)	[Extractable complex formed only on heating					]
25	Mn(II) b	5.66	6.4	6.1	6.8 a	11	12
26	Fe(III)	1.00 c	5.3 c	1.7 ac	3.2 ac	9.5 c	11 ac
27	Co(II)	3.21	4.2	3.2	5.2 a	10.1	11 c
28	Ni(II)	2.38 b	5.0 c	3.2 c	---	11.5 c	12.5 bc
29	Cu(II)	1.37 c	3.6 c	---	3.8 c	9.0 ac	10.2 c
30	Zn(II)	3.30 ab					
31	Ga(III)	1.07	4.4 c	---	5.5 ac	9.9 c	10.8 c
32	Sr(II)	12.06	ppt.	10.4 c		[No Extraction]	
40	Zr(IV)	1.01	4.7	3.0 a	>9	>9	>9
41	Nb(V)	[Quantitative excess oxine pH 2.8-10.5]					
42	Mo(VI)	[Quantitative pH 1 to 4, No Extraction pH > 8]					
46	Pd(II)	0 b			b	b	b
47	Ag(I)	6.51 n	6.5 n	6.5 n	[15% Extr. pH >5		]
48	Cd(II)	4.65 c	5.5	4.9	10 a	[No Extraction]	
49	In(III)	1.54 c	4.3 c	2.2 c	8.5 c	10.2 c	10.9 ac
56	Ba(II)	11	ppt.	---	---	[No Extraction]	
57	La(III)	6.46	8.4	7.5	11 c	11 c	11 c
74	W(VI)	b	[partial Extr.]		[Quantitative pH 2.5-3.5, S]		
80	Hg(II)	[Partial Extraction	]		[Not Extracted		]
81	Tl(III)	2.0 c	2.8 c	2.0 c	9.0 bc	11.3 bc	12 bc
82	Pb(II)	5.04	6.2	5.5	9.5	[No Extraction	]
83	Bi(III)	2.13	4.8	3.2 a	7.8 a	10	11 a
90	Th(IV)	2.91	6.8	6.2	>7	>7	>9
92	U(VI)	2.60 a	7.4	6.7	5.4 a	6.1 a	4.7 a

Notes: a. Curve of extraction vs. pH was not ideal in some manner.
        b. Requires special handling. See original paper for details.
        c. Data from other than 0.10 or 0.010 M solutions.

FIGURE III

EFFECT OF pH ON THE EXTRACTION OF Tl(IV) by
8-HYDROXYQUINOLINE. Reference 86.

From J. Stary, Anal. Chim. Acta, 28: 132 (1963); reprinted by permission.
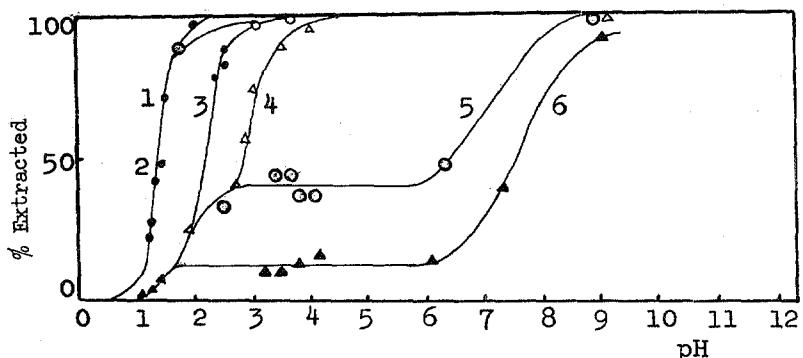
1. No added reagent.

2. 0.010 M Tartaric acid.

3. 0.010 M Nitrilotriacetic acid.

4. 0.010 M Oxalic acid.

5. 0.010 M Ethylenediaminetetraacetate.

6. 0.010 M 1,2-diaminocyclohexanetetraacetic acid.

tetraphenylarsonium chloride. Sommer used a chloroacetic acid buffer to maintain the pH of the aqueous phase at 2.7, added 1% aqueous polyphenol solution and solid tetraphenylarsonium chloride. He reported no analytical interference from Ni(II), Co(II), Mn(II), Zn, Cd, Mg, Sr, Ca, Ba, Al, Th, or tungstate. Zirconium precipitated, Fe(III) extracted somewhat except with 2,3-dihydroxynaphthalene, U(VI) and Nb extracted, Ta, molybdate, and V(V) interfered.

Other Solvent Extraction Systems

In the book "Solvent Extraction of Metal Chelates," Stary reviews the literature and gives a systematic presentation of several extraction

FIGURE IV

pH DEPENDENCE OF THE SOLVENT EXTRACTION OF TITANIUM(IV)
AND NEIGHBORING ELEMENTS. Reference 89

From J. Stary, <u>The Solvent Extraction of Metal Chelates</u>, Pergamon Press, Inc., New York, 1964; reprinted by permission.


0.1 M Acetylacetone in Benzene

0.1 M Benzoylacetone in Benzene

0.1 M Dibenzoylmethane in Benzene

Figure IV continued

0.005 M Cupferron in Chloroform
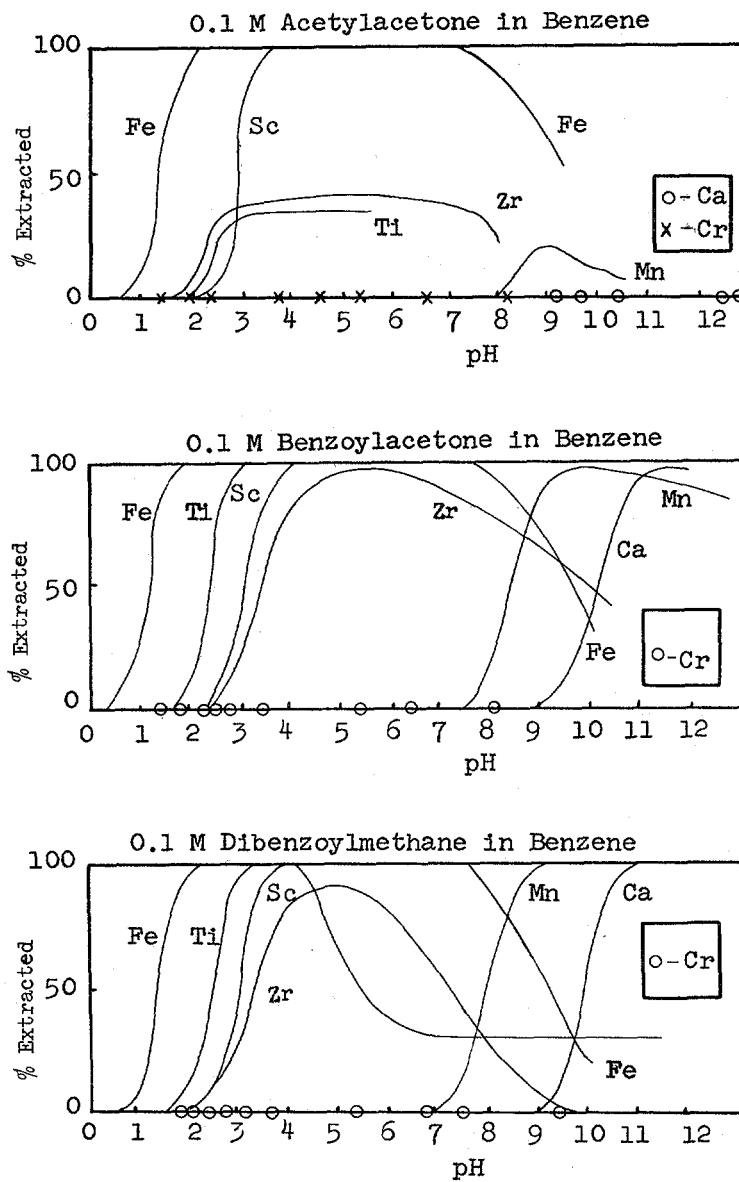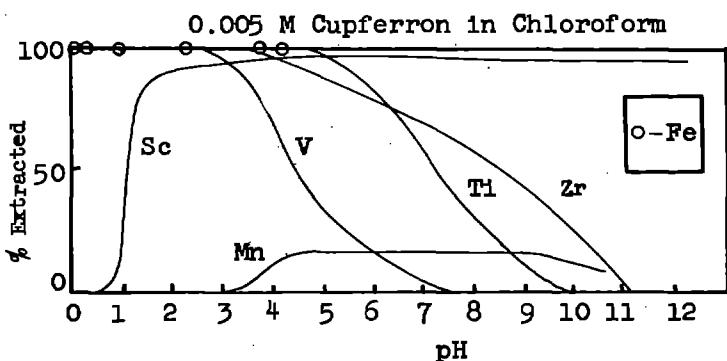
systems.[89] Figure IV shows the behavior of titanium(IV) and its neighboring elements in these systems.

Another systematic review of solvent extraction systems may be found in the 1962 report, JAERI 1047, edited by Ishimori.[90] He shows the behavior of about 60 elements in phosphorous derivative extraction systems and also in some amine and arsonium systems. Figures V and VI are reproduced from this review and demonstrates the behavior of titanium(IV) and its neighboring elements in representative systems. The abbreviations used are: TBP - tri-n-butylphosphate, TBPO - Tri-n-butylphosphine oxide, TOPO - Tri-n-octylphosphine oxide, HDEHP - bis-2-(ethylhexyl)phosphate, TIOA - tri-iso-octylamine.

Thin Layer Chromatography

In working on his doctorate thesis, Brinkman[91] used thin layer chromatography with liquid anion exchangers adsorbed on silica gel and mounted on microscope slides as a means of conveniently determining the ammine extraction behavior of many elements. He selected Primene JM -T, Amberlite LA-I, and Alamine 336 as representing weakly to strongly adsorbing ammines respectively. Hydrochloric acid concentrations of 1 to 12 molar served as solvent. Although most elements showed thin layer chromatographic behavior similar to their

35

FIGURE V

Acid Dependence of Solvent Extraction of Titanium(IV) and Adjacent Elements. Reference 90.

From T. Ishimori, Japanese Atomic Energy Research Institute Research Report No. JAERI-1047, 1963; reprinted by permission.

HCl -- 100% TBP

(CrO$_4^-$ extractable   MnO$_4^-$ extractable)

HNO$_3$ -- 100% TBP

Figure V - Continued

1% TBPO (Toluene) -- HCl

1% tetrabutylmethylenediphosphonate (Xylene) -- HNO₃
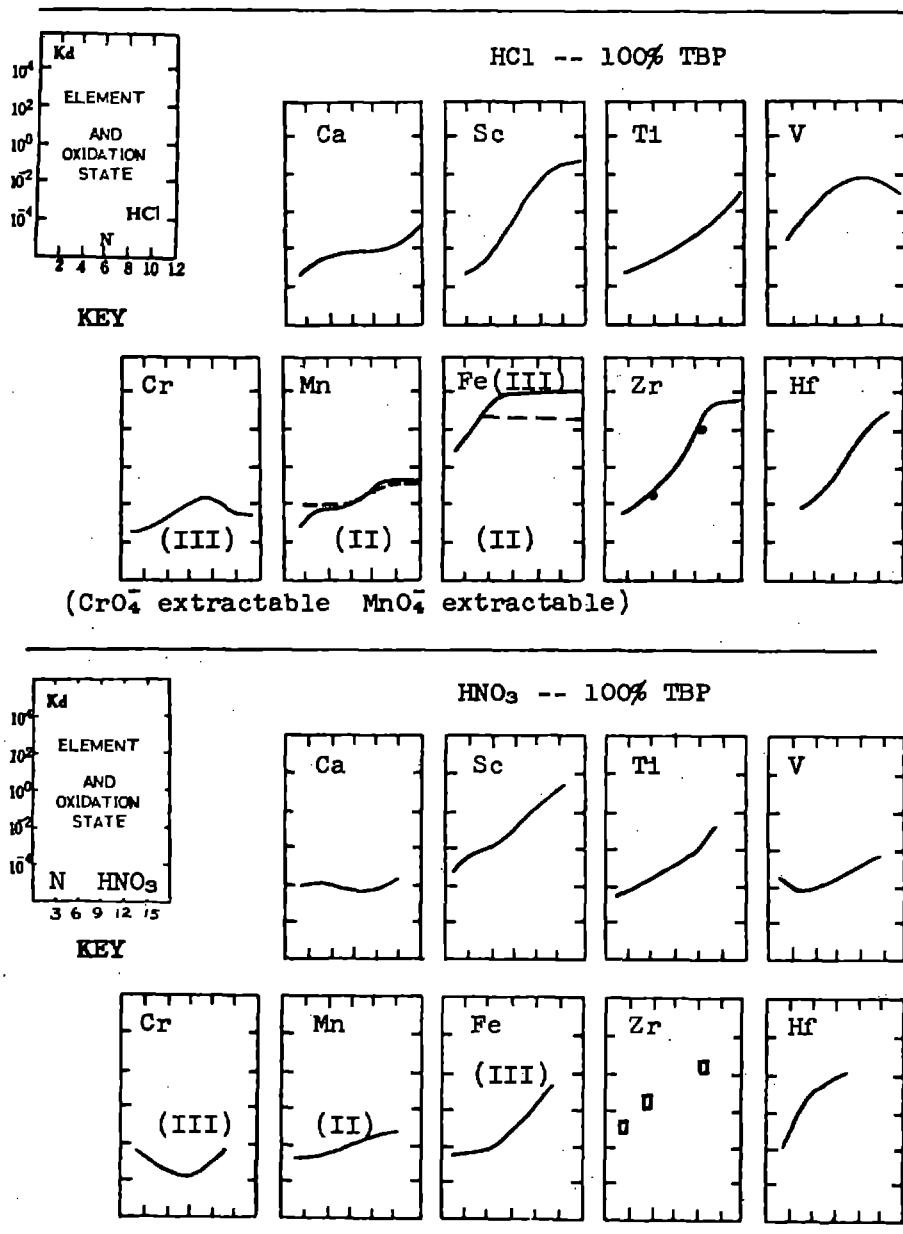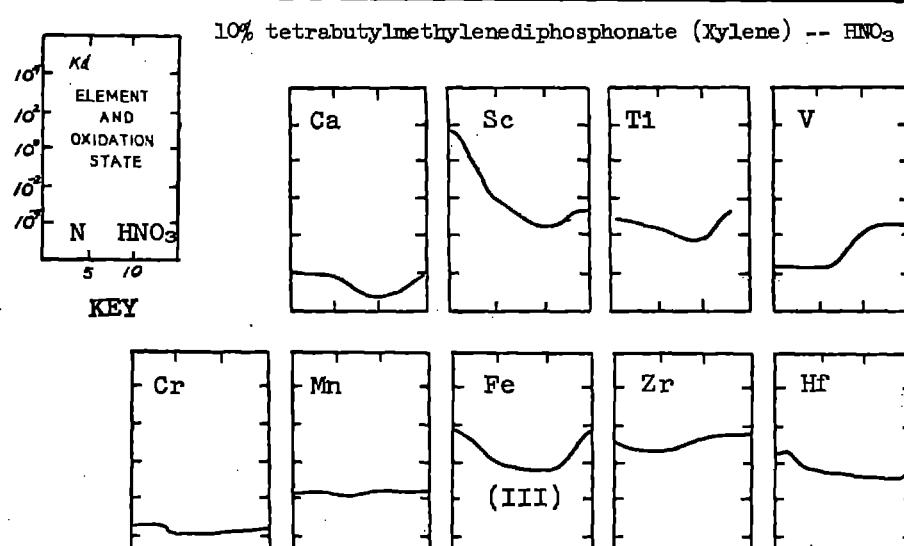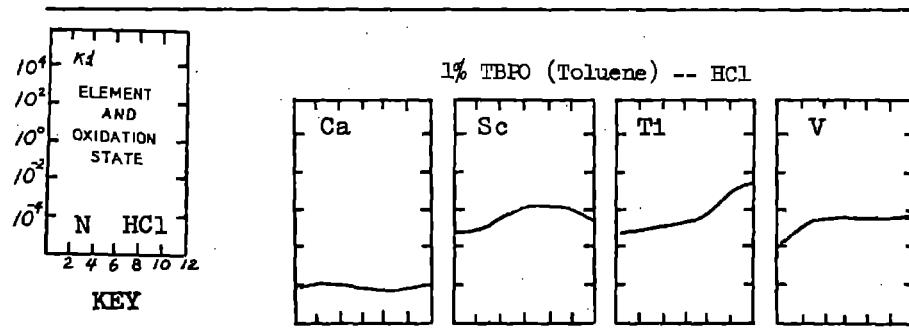
Figure V - Continued
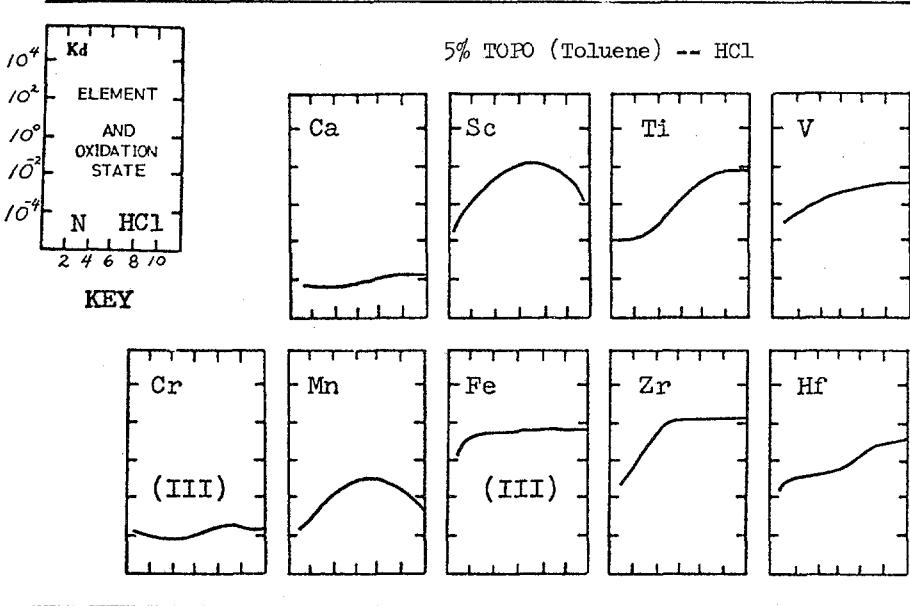
extraction behavior, titanium(IV) always chromatographed as though it were on the silica gel with no exchanger added. This behavior was distinctly different from the neighboring elements, and may offer a means of separation for titanium.

C.   Ion Exchange Separations

The ion exchange behavior of titanium follows rather directly from its general chemistry. Complexing and hydrolysis vary the ionic charge on the titanium species and hydrolytic precipitation can cause severe difficulties in the elution of titanium(IV).

Cation Exchangers

The cation exchange behavior of titanium(IV) species has been well reviewed by both Samuelson[92] and Strelow.[93][94][95] Strelow has studied the adsorption of titanium(IV) and 42 to 48 other cations on purified Dowex 50 cation resin (AG 50-W-X8) from HCl,[93] HNO_3,[95] and H_2SO_4.[95] Tables VII, VIII, and IX show selected values of weight dis-

FIGURE VI

Acid Dependence of Solvent Extraction of Titanium(IV) and Adjacent Elements Reference 90.

From T. Ishimori, Japanese Atomic Energy Research Institute Research Report No. JAERI-1047, 1963; reprinted by permission.


50% HDEHP (Toluene) -- HCl

5% TIOA (Xylene) -- HCl

Figure VI - Continued

10% Amberlite (Xylene) LA-1-HCl

10% Primene JM-T (Xylene) HCl

Figure VI - Continued

0.1 M dimethylbenzylphenylammonium
chloride (Chloroform) - HCl
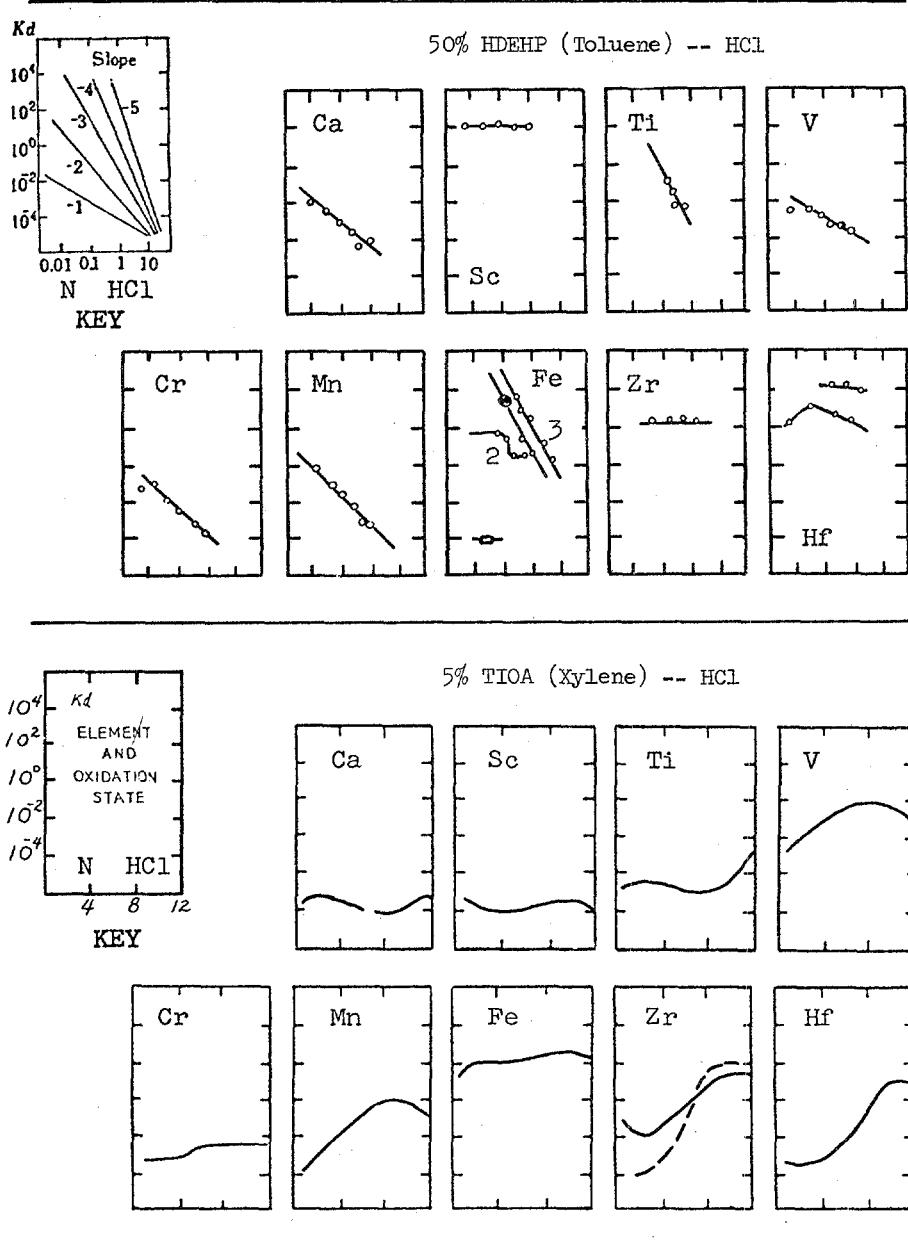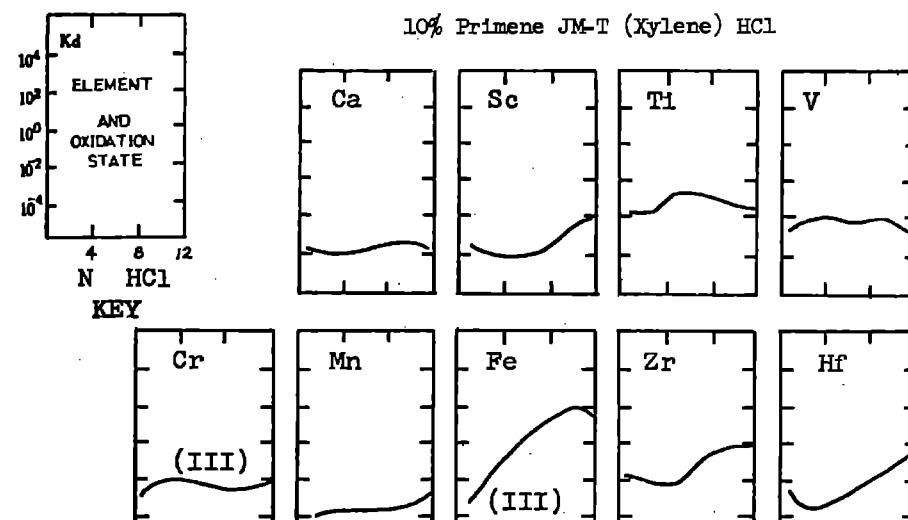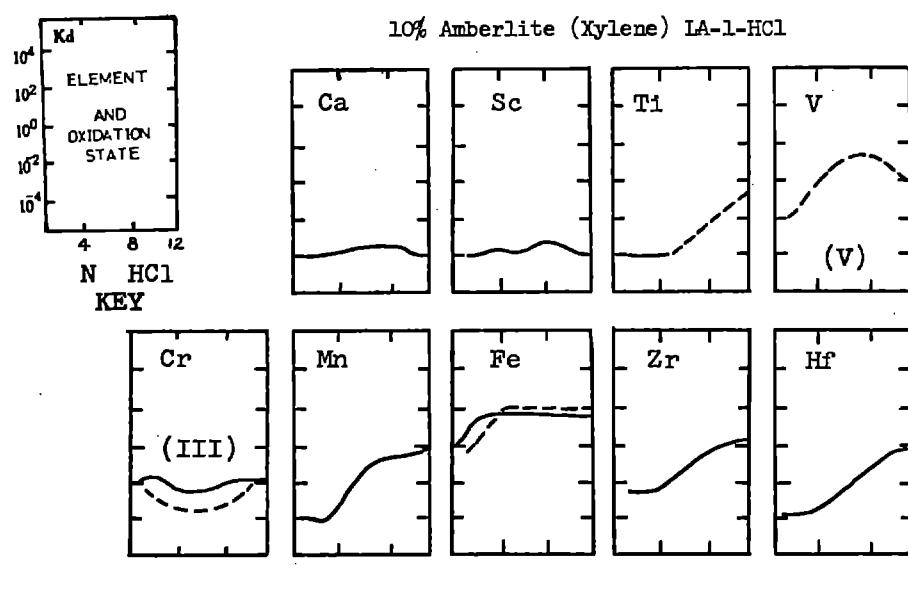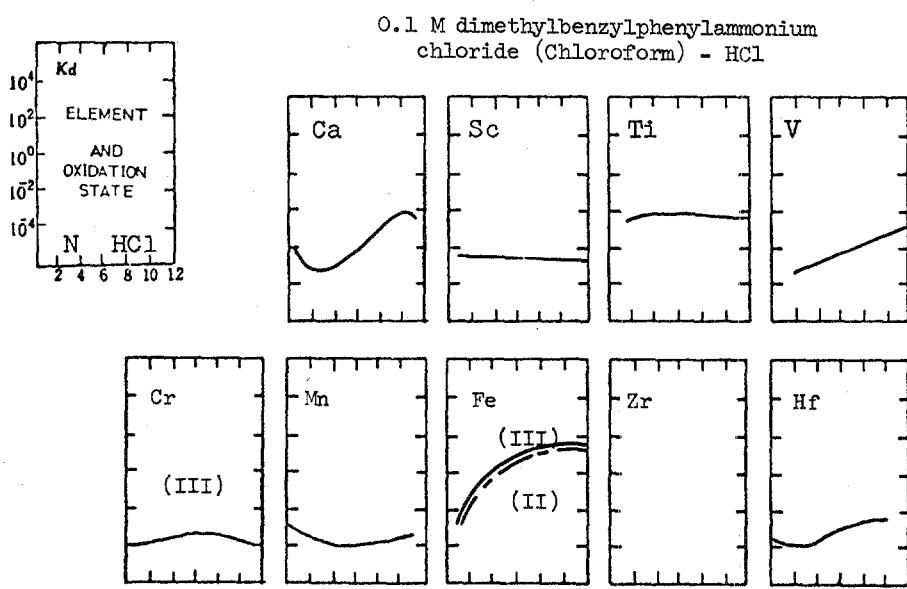
tribution coefficients, K_D, from these studies. The cation equivalents to

resin equivalents ratio, q, was maintained at 0.4 so that the coefficients

reported were compatible within, and between, the systems studied.

Table X shows selected results of a similar study using slightly

acid ammonium sulfate solutions.[96]

Strelow illustrated the usefulness of these values with a series

of separations. Columns containing 20 g of resin (100 meq.) were

loaded with 1 meq. of each of several metal ions. A solvent in which

K_D for the ion to be eluted was less than 10, and those for the ions

to be retained were greater than 30 was selected. Elution with 200

to 400 ml removed the desired ion and another appropriate solvent

was used to elute each successive ion. This technique was applied to

a separation of titanium(IV) from a mixture by adsorption from 0.15

M H_2SO_4 containing 1% H_2O_2.[94] Elution with 0.25 M H_2SO_4 containing

1% H_2O_2 removed Nb, V(V), Mo, Ta, and W. An elution with 0.5 M H_2SO_4

TABLE VII

Cation Exchange - K_D at Various HCl Concentrations
(Dowex 50). Reference 93.

From F. W. E. Strelow, Anal. Chem., 32: 1185 (1960); reprinted by permission.

Cation	Concentration of Hydrochloric Acid
	0.1 M	0.2M	0.5M	1.0M	2.0M	3.0M	4.0M
Ca	3200	790	151	42.29	12.2	7.3	5.0
Ti(IV)	$>10^4$	297	39	11.86	3.7	2.4	1.7
V(IV)		230	44	7.20			
V(V)	13.9	7.0	5.0	1.10	0.7	0.2	0.3
Cr(III)	1130	262	73	26.69	7.9	4.8	2.7
Mn(II)	2230	610	84	20.17	6.0	3.9	2.5
Fe(II)	1820	370	66	19.77	4.1	2.7	1.8
Fe(III)	9000	3400	225	35.45	5.2	3.6	2.0
Al	8200	1900	318	60.8	12.5	4.7	2.8
Y	$>10^5$	$>10^4$	1460	144.6	29.7	13.6	8.6
Zr	$>10^5$	$>10^5$	$\sim 10^5$	7250	489	61	14.5

TABLE VIII

Cation Exchange - K_D at Various HNO_3 Concentrations
(Dowex 50). Reference 95.

From F. W. E. Strelow, R. Rethemeyer, and C. S. C. Bothma, Anal. Chem., 37: 106 (1965); reprinted by permission.

Cation	Concentration of Nitric Acid
	0.1M	0.2M	0.5M	1.0M	2.0M	3.0M	4.0M
Ca	1450	480	113	35.3	9.7	4.3	1.8
Sc	$>10^4$	3300	500	116	23.3	11.6	7.6
Ti(IV)	1410	461	71	14.6	6.5	4.5	3.4
V(IV)	495	157	35.6	14.0	4.7	3.0	2.5
V(V)	20.0	10.9	4.9	2.0	1.2	0.8	0.5
Cr(III)	5100	1620	418	112	27.8	19.2	10.9
Mn(II)	1240	389	89	28.4	11.4	7.1	3.0
Fe(III)	$>10^4$	4100	362	74	14.3	6.2	3.1
Al	$>10^4$	3900	392	79	16.5	8.0	5.4
Zr	$>10^4$	$>10^4$	10^4	6500	652	112	30.7

42

Concentration of Sulfuric Acid							
Cation	0.05 M	0.1 M	0.25 M	0.5 M	1.0 M	1.5 M	2.0 M
Sc	5600	1050	141	34.9	8.5	4.4	3.4
Ti(IV)	395	225	45.8	9.0	2.5	1.0	0.4
V(IV)	1230	490	140	46.6	11.5	2.4	0.4
V(V)	27.1	15.2	6.7	2.8	1.2	0.7	0.4
Cr(III)	198	176	126	55	18.7	0.9	0.2
Mn(II)	1590	610	165	59	17.4	8.9	5.5
Fe(II)	1600	560	139	46.0	15.3	9.8	6.6
Fe(III)	>10^4	2050	255	58	13.5	4.6	1.8
Al	>10^4	8300	540	126	27.9	10.6	4.7
Zr	546	474	98	4.6	1.4	1.2	1.0

	Conc. NH_4SO_4 in 0.025 M H_2SO_4			
Ion	0.20 M	0.30 M	0.50 M	1.0 M
Sc	9.5		4.5	2.5
Ti(IV)	4.5	3.5	2.5	1.5
V(IV)	18	8.2	4.0	1.9
Cr(III)	270	77	11	0.2
Fe(III)	23	7.7	3.8	1.8
Al	85	35	8.0	2.5
Zr	< 1	< 1	< 1	< 1

removed Ti(IV), Zr, and U(VI). Ga, Fe(III), Hg(I), and Ag remained on the column. This use of H_2O_2 to prevent hydrolysis did not appear to change the distribution of titanium(IV) appreciably. Several authors have found the addition of hydrogen peroxide to be useful in the ion exchange separation of titanium.

Strelow also developed a convenient cation exchange method for separating scandium and the rare earths from titanium and most other metal ions of the insoluble hydroxide group.[97] After being loaded on to Dowex-50 from 0.1 M HCl solution, titanium(IV) could be eluted with 1.75 M HCl. Scandium and the rare earths were then eluted with 3.0 M HCl.

According to Fritz[98] 0.5 M HBr will not effect removal of titanium(IV) from a Dowex-50 column. Since the neighboring elements are not removed by HBr either, this solvent will be applicable only to the removal of other elements from the first transition series elements. As would be anticipated, 0.1 or 1.0 M HF rapidly removed titanium(IV) from the same resin[99]. Co(II), Cr(III), Mn(II) and

V(IV) were not eluted by 0.1 M HF. Al, Sc, Nb and Zr were eluted with the titanium.

Table XI is a compilation of some cation exchange separations which have been reported in the literature. The references are primarily from Samuelson[92] and Strelow (1963).[94]

Anion Exchangers

In hydrochloric acid, titanium(IV) is a member of the group of elements which are very slightly adsorbed by anion exchange resins from dilute acid but are more strongly adsorbed from strong acid.[118] Hydrolysis problems are reported if the hydrochloric acid concentration is less than 9 M. Since Sc(III), V(IV), Cr(III), and Mn(II) are very slightly adsorbed from HCl at any concentration while Ti(IV) is adsorbed from concentrated HCl, several separation schemes have

44

TABLE XI
Summary of Cation Exchange Separations of Titanium

Origin	Resin	Separated From	Eluent	Reference
Solutions	Dowex 50	Th	Ti, Zr-1% Citric Acid $Th-NH_4$ Citrate	(100)
Solutions	KU-2	Zr	Ti- 1M HCl Zr - 4 M HCl	(101)
	Poly. Styr. sulfonate	Al	Ti-EDTA - H_2O_2 - pH 1-3 (Al ads)	(102)
Ti alloys	KU-2	Al	Ti - 0.75 M HCl & H_2O_2 Al - 2 M HCl	(103)
Solutions, Std. Clay	AG-50 W	Zr, Th	Ti - 2 M HCl Zr - 5 M HCl	(104)
Solutions	KU-2	Fe(III)	Ti - 0.25 M HCl Fe - .4 M HCl (loaded from 0.25 M HCl)	(105)
	SBS	Fe(III)	Ti - 0.4 M HCl Fe - 4 M HCl	(106)
Solutions	SBS	Cr(III)	Ti - EDTA + HCl (Cr held)	(107)
Solutions	KU-1	Mn(II)	Mn - 0.5 M HCl Ti - 4 M HCl	(108)
	IR -120 H	U(IV)	Ti - 2 M HCl $U(IV) - 1 M H_2SO_4$	(109)
Solutions	SBS	W	$W - pH 5 H_2SO_4 + H_2O_2$ $Ti - 10\% H_2SO_4$	(110)
Solutions & Steels	SBS	V(V), Mo W	$V, Mo, W - pH 1 H_2SO_4 + 1\% H_2O_2$	(111)
Solutions	SBS	Nb	$Nb - 0.3 N H_2SO_4 + 5\%$ citric	(112)
Solutions	KU-2	Nb	$Nb - 0.3 M HCl + 0.2\% H_2O_2$	(113)
Limonite	Poly Styr Sulfonate	Fe	Fe - 2 M KCN $Ti - 10\% H_2SO_4$	(114)
Steels	Dowex-50 W	Fe(III), Si Cu(II), Ni, Cr(III), W Mn(II), Nb Sn(IV)	$Others - 0.5\% H_2SO_4$, $Ti, V(IV) - 1\% H_2SO_4 +0.37\%$ Ammonium citrate	(115)
Steels	formaldehyde Resorcinol	V(V)	$V-pH 1 + H_2O_2$ Ti, Fe - acid	(116)
Solutions	Dowex-50	V(V), Fe(III)	$V - 0.01 M HClO_4$, $1\% H_2O_2$ $Ti - 1.0 M HClO_4$, $1\% H_2O_2$ Fe - 2 M HCl	(117)

been developed using these facts. Vanadium(V) and chromium(VI) are much more strongly adsorbed than titanium(IV). Kraus,[119] for instance, separated a mixture on Dowex X-1 by eluting V(IV) with 12.1 M HCl, Ti(IV) with 9.1 M HCl, and Fe(III) with 1.0 M HCl. The systematic studies of Nelson, Rush, and Kraus,[119,120] indicate that the adsorption of titanium(IV) from concentrated HCl could be the basis for many other separations.

The labile fluoride complexes of titanium(IV) are also useful in anion exchange separations. Since fluoride is useful in the dissolving of titanium materials, the use of this medium is reasonable in spite of the difficulties incumbent in the use of plastic ware and the extra care required by fluorides. Dowex-1 has been used in comprehensive studies of anion exchange of metal ions from 1.0 M HF.[120] Figure VII shows some of the results of this work. The values given are volume distribution coefficients, D_V.

Nelson, Rush and Kraus[120] also specifically illustrated the separation of V(IV) from Ti(IV) in HCl-HF systems by both anion and cation exchange to show the reciprocal relationship between these methods. Figure VIII is taken from this work.

Faris[121] has studied the elution of 50 elements from Dowex-1 (X-10) with various hydrofluoric acid concentrations. Figure IX shows the behaviour of some elements of interest expressed in terms of weight distribution coefficients.

Other studies[122] show that, if 0.3% hydrogen peroxide is added to prevent hydrolysis, titanium(IV) is very slightly adsorbed from 0.2 to 4.0 N sulfuric acid. The potential utility of this system would be in quickly separating slightly adsorbed ions like Ti(IV), V(IV), and Cr(III) from more strongly held ions such as Zr(IV), Ta(V), Mo(VI), and Cr(VI).

In addition to these systematic studies of anion exchange behavior in mineral acid systems, a good deal of use has been made of titanium complexes to

46

FIGURE VII

Anion Exchange Adsorption of Some Elements from
Hydrochloric Acid and Hydrochloric Acid-Hydrofluoric
Acid Mixtures. Reference 120.

From F. Nelson, R. M. Rush, and K. A. Kraus, J. Amer. Chem. Soc., 82: 339
(1960); reprinted by permission.
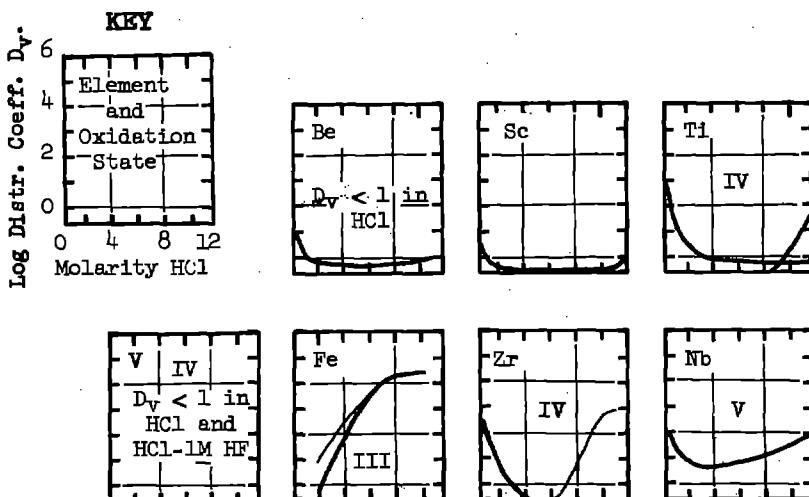
Adsorption of some elements from HCl and HCl-HF
solutions (0.1 < M HCl < 12): ————, distribu-
tion coefficients in absence of HF; ————,
distribution coefficients in HCl-HF mixtures
(usually 1 M HF except Zr(IV), Hf(IV), Nb(V) and
Ta(V), where M = 0.5).

effect anion exchange separations for analytical purposes. In most of the

analytical separations, the only indication of purity is the lack of interferences

with a colorimetric test. Some of these separation procedures are outlined in

Table XII. Again, most of the references are taken from Samuelson[90] and

Strelow.[92]

D. Paper Chromatography Separations

Although usually considered as slow, paper chromatography can offer

a reasonably rapid and convenient means of separating metal ions. This method

has been used to separate fission products, and titanium(IV) has been separated

from Al, Fe, Zr,,and other elements by using such varied solvent systems as

TABLE XII

A Summary of Anion Exchange Separations of Titanium

Origin	Resin	Separated From	Eluent	Reference
Solutions	Dowex 1	V(IV) Fe(III)	V - 12.1 M HCl Ti - 9.1 M HCl Fe - 1.0 M HCl	(119)
Minerals	IRA 400	Fe(III) Cr(III) Ni, Co(II)	Fe - 2% Ascorbic acid pH 4;Ti - 1 N H_2SO_4	(123)
Fe Alloys	Dowex-1	Mo, V Zr	Ti - 0.1 N H_2SO_4 + 3% H_2O_2	(124)
Natural Water	Dowex-1 (ascorbate)	Ca, Mg, Fe(III), etc.	Many - 1% Ascorbic pH 4-5 Many - 0.1 N H_2SO_4 + 0.25 M NaF Ti- 0.1 N H_2SO_4 + 3% H_2O_2	(125)
Silicate Rocks	Dowex-1	R.E.,PO_4^{3-} Fe,Al,Be Group II, W, Zr	Others - 0.1 N H_2SO_4 + 0.25 M NaF Ti - 0.1 N H_2SO_4 + 3% H_2O_2 Zr - 4 M HCl	(126)
Minerals (in HF)	Dowex-1	Group II Zr,Be,Fe Ni,Co,Zn, Mn,Th,V,W Mo,U,Sn,Sb	Many - 0.1 N H_2SO_4 + 1% NaF (Rinsed 0.1 N H_2SO_4) Ti - 0.1 N H_2SO_4 + 3% H_2O_2 (some separation in Na_2CO_3 leach)	(127)
Ti Target	Dowex-1	Sc, V(IV)	Sc- 0.1 M Oxalic, 0.1 M HCl V - 0.1 M Oxalic, 0.4 M HCl Ti - 0.1 0.1 M HCl (Carrier Free Sc & V)	(128)
Hi Temp Alloys	Dowex-1	Mo,W, Nb	Ti - a) 25% HCl, 5% HF or b) 50% HCl, 10% HF	(129)
Steels	IRA 400	Fe,Cr,Ni V, Mo, Co Mn, W, Nb	V(V), Fe - 0.12 M HCl + 0.4 M HF Ti - 3 M HCl (No interference H_2O_2 Color)	(130)
HF Solutions	EDE-10P	Nb Ta Fe	Fe Nb(.9) - 1M HCl, 0.05 M HF Ti Nb(.1) Ta(.06) - 3 M HCl Ta(.94) - 9M HCl, 0.05 M HF	(131)
High Temp Alloys	Dowex-1	Nb Ta Mo Sn Fe	Ti Zr - 50% HCl, 10% HF Fe Mo Sn - 7% NH_4Cl, 12.5% HCl, 20% HF (Followed cupferron pptn.)	(132)

TABLE XII (continued)

Origin	Resin	Separated From	Eluent	Reference
Steels	Dowex-1	Nb Ta W Mo	V Ti Zr - 1.5 M HCl, 0.5 M Oxalic Nb - Same later Ta-3 M HCl, 0.5 M Oxalic W -4 M HCl, 0.1 M Citric Mo - 1.9 M NH_4Cl, 0.44 M ammonium citrate	(133)
Ti Target	Dowex-1	V(IV), Sc	V - 0.5 to 2.5 M HF Sc - 15 M HF (both carrier free)	(134)
Alloys	IRA-400	Ta Nb	Ti - 20% HF, 40% HCl Nb - 5% HF, 25% HCl Ta - 75% HF, 25% HCl	(135)
Solutions	An-2F	Mn(II)	Mn - 8 M HCl Ti adsorbed (1:1 should elute)	(136)
Alloys	Dowex-1	Zr Hf Mo	Ti - 6% H_2SO_4, 0.025 M Oxalic Zr Hf - 10% H_2SO_4 0.025 M Oxalic Nb - 20% H_2SO_4, 0.10 M Oxalic Mo - 20% H_2SO_4	(137)
Silicate rocks	Dowex-1	Fe Mn Ca Mg Others	Others - 3.5% Sulfosalicylic acid Fe - Conc. HCl Ti - 1:1 HCl	(138)

pentanol-benzene-HCl; butanol-HCl; methyl acetate-HNO3-water; and ether-methanol-HCl[20].

Qureshi and co-workers have developed a method for quantitatively separating titanium from synthetic mixtures of over 17 cations including Fe(III), Cr(III), Al, V(IV), and $UO_2{}^{2+}$[139,140]. About one lambda samples of 0.1 M metal ion solutions in 4 M HCl were put on 15 × 3 cm strips of No. 1 paper and hung in glass jars. About one hour was required for the solvent to travel their usual 12.5 cm distance. Their most versatile solvent system was formic acid-HCl-acetone, 3:5:2. Citrate and tartrate did not interfere because of the high hydrochloric acid concentration. Aqueous 5% chromotropic acid was used to establish the location of the titanium.

49

FIGURE VIII

Ion Exchange Separation of
Titanium and Vanadium. Reference 120.

From F. Nelson, R. M. Rush, and K. A. Kraus, J. Amer. Chem. Soc., 82: 339 (1960); reprinted by permission.
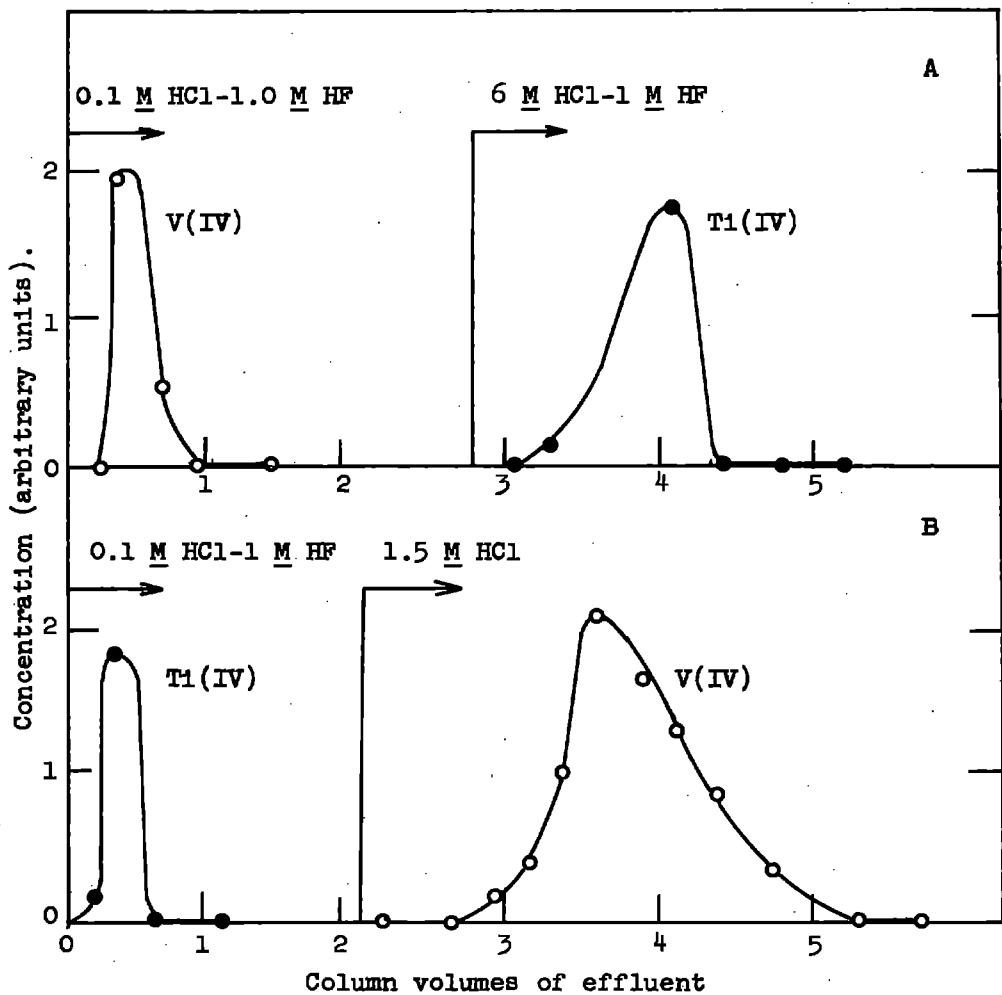
Separation of Ti(IV) and V(IV):   A, anion exchange; B, cation exchange.

FIGURE IX

Anion Exchange Adsorption from

Hydrofluoric Acid. Reference 121.

From J. P. Faris, _Anal. Chem._, 32: 520 (1960); reprinted by permission.

KEY

Log Distr. Coeff.

4
3
2
1
0

0 5 10 15 20 25
Molarity HF

Sc — III

Ti — III, IV

V — V, IV

Cr — VI, III

Mn — VII, No Ads.

Fe — III, II

Zr — IV

Nb — V

Mo — VI
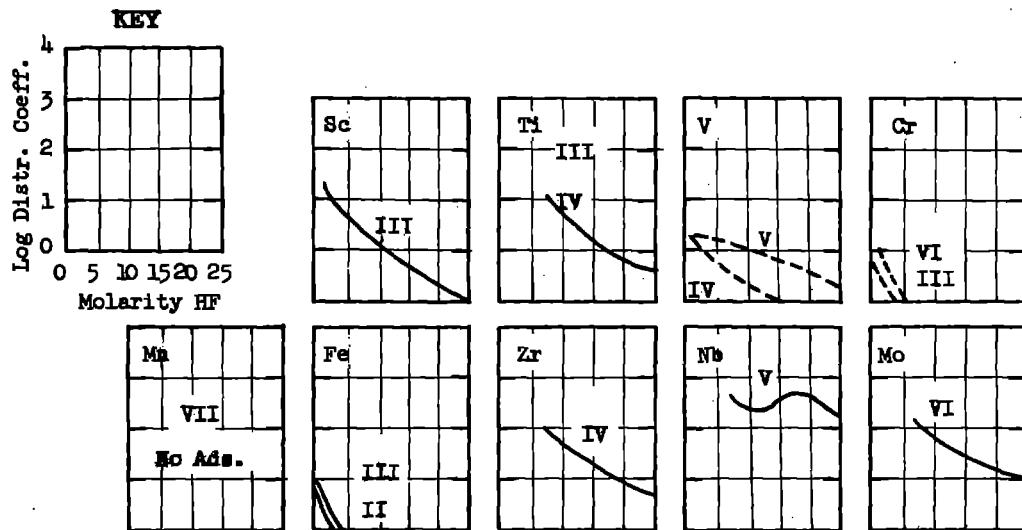
Roman numerals refer to oxidation state.

No Ads. - No adsorption from 1 M - 2^4 M HF.

9. DISSOLUTION OF TITANIUM-CONTAINING MATERIALS

A. Titanium Metal and Alloys

Titanium metal will dissolve in non-oxidizing acids, such as hydrofluoric, sulfuric, hydrochloric, or fluoroboric. Addition of hydrogen peroxide or nitric acid will then ensure oxidation to Ti(IV). Hydrofluoric acid reacts vigorously, and Scheffer[14] recommends adding HF slowly and dropwise to a sample of titanium metal or alloy which is covered with water. Usually hydrofluoric acid is used in conjunction with dilute sulfuric acid, although titanium will dissolve in sulfuric acid alone if the mixture is heated to fumes of SO_3, yielding $Ti(SO_4)_2$ and SO_2. The reaction with fluoboric acid is complete even in cold solution, and is considerably less violent than with hydrofluoric acid. Hydrochloric acid will

51

dissolve the metal at a moderate rate with heating. Titanium tri-chloride is formed if the solution is protected from oxidation. Dilute oxidizing acids usually attack the metal very slowly to form an insoluble oxide, or acid film.

Steels containing titanium may be dissolved in 1:1 HCl and the residue treated with one of the following: HF and $HClO_4$, 55% $HClO_4$, HNO_3, aqua regia, HCl, HNO_3 and H_2SO_4. Aluminum metal may be treated with NaOH, then with HNO_3 and H_2SO_4.

B. Titanium Dioxide

Scheffer[14] suggests a satisfactory medium for dissolution of 0.5 g of titanium oxide as 8 g of ammonium sulfate and 20 ml of concentrated sulfuric acid. Sodium or potassium sulfates are somewhat less satisfactory. Sulfuric acid alone reacts too slowly to be useful. Hot hydrofluoric acid reacts slowly with titanium oxides and more HF must be added during dissolution. Scheffer recommends addition of 10 ml concentrated sulfuric acid per gram of titanium dioxide when dissolving the oxides with HF.

The oxide may also be fused with potassium pyrosulfate in a porcelain crucible at 800° C. Fusion with sodium carbonate should be followed by dissolution in hot 6M HCl.

C. Salts

The halides of titanium are soluble in water, though hydrolysis may occur. Most double salts and titanates are soluble in hydrochloric acid. The sulfate $Ti(SO_4)_2$ is soluble in cold, dilute sulfuric acid but at low acidity hydrolyzes to an insoluble basic sulfate or hydrated oxide.

D. Ores

Ores such as ilmenite, rutile, or others containing mainly iron, silicon, calcium, magnesium and aluminum may be treated with 3:1 sulfuric acid and an equal volume of hydrofluoric acid in a

platinum dish or Teflon beaker. Alternatively, fusion with potassium

pyrosulfate may be used. Depending on the nature of the ore, fusion

with NaOH, NaOH and Na_2CO_3, Na_2O_2, 10:1 Na_2CO_3-KNO_3, KHF_2, 1:6 KF-$Na_2S_2O_7$,

or borax may be effective.[74] Iron ores can be dissolved in HCl and

H_2SO_4 and the residue treated with HF and H_2SO_4 or the sample can be

treated with H_2SO_4 and H_3PO_4.[74]

E. Biological Samples

The sample may be treated with concentrated sulfuric and nitric

acids and heated. Small amounts of ammonium persulfate may be added

if necessary to speed up oxidation. If dissolution of titanium has not

occurred, ammonium sulfate may be added and the solution boiled.[14]

Many organic samples can be brought into solution by burning in air or

oxygen, followed by treatment of the resulting ash by the ammonium

sulfate-sulfuric method described for titanium dioxide, or by fusion

of the ash with potassium pyrosulfate. For small samples, direct fusion

of the sample with potassium pyrosulfate in a platinum crucible is

satisfactory, followed by dissolution in sulfuric acid. Organic

samples may also sometimes be dissolved in concentrated nitric acid

followed by careful addition of 72% perchloric acid.[141]

V. Hazards and Precautions in Handling
Titanium-Containing Materials

Neither the metal nor most compounds of titanium are toxic or

explosive. The metal is rated as physiologically inert and the dioxide

is considered as a "nuisance" only (142). Titanium metal under strong

oxidizing conditions is pyrophoric. It is, in fact, the only element

which will burn in nitrogen.[5] The tetrachloride of titanium evolves

copious white fumes of titanium hydrous oxide and hydrochloric acid

on exposure to moisture. For this reason, titanium tetrachloride is

listed as highly toxic to the eyes and lungs, and highly irritating to the skin. Dissolution of titanium metal in hydrofluoric acid may become violent, as mentioned earlier.

VI. Counting Techniques

The titanium isotopes of interest for radiochemistry are Ti^{44}, Ti^{45}, and Ti^{51}. Titanium-44 has all of the attributes of an excellent tracer, namely, it has a long half-life (48 y), is relatively easy to detect, and is commercially available (as a cyclotron-produced radionuclide). Titanium-45 (3.1 hour) also may have some use as a tracer for applications requiring a shorter half-life. Titanium-51 has a half-life of only 5.80 minutes, and is of interest chiefly because it is produced from neutron capture by titanium-50 (5.34% abundance), and as such is useful for determination of titanium by activation analysis. The half-lives of the other titanium isotopes are too short to be of general interest. Titanium-42 has been recently reported as having a half-life of 0.25 ± 0.04 sec and decays to the 611.5 keV state of scandium-42.[144]

1. TITANIUM-44

Titanium-44 decays by electron capture to Sc^{44}, accompanied by the emission of 68 and 78 kev gamma rays. Scandium-44 in turn decays by positron emission or electron capture with a 3.92 hour half-life to stable Ca^{44}. Thus Ti^{44} may be detected by either gamma spectrometry or beta counting of Sc^{44}.

A. Gamma Spectrometry

The detection of Ti^{44} will be discussed in some detail because of its importance as a tracer and the fact that Ti^{44}-Sc^{44} is a useful source for energy calibration of NaI(Tl) detectors. Titanium-44 may be determined directly with a small NaI(Tl) detector by measuring the 68 and 78 kev gamma rays. The advantage of this technique is that a

relatively inexpensive NaI(Tl) crystal is adequate; a thickness of 0.22 cm should absorb 90% of the radiation at these energies.[145] Although the background in crystals of this thickness is generally low, a further reduction can be obtained by counting the sample between two such crystals, requiring gamma-gamma coincidence. An even greater improvement in sensitivity is obtainable by two-dimensional spectrometry.

In the presence of gamma radiation of higher energies, it may be preferable to measure the gamma radiation from Sc^{44}. This consists of 0.51 MeV gamma rays from positron annihilation, together with a 1.16 MeV gamma ray. As seen from Figure X, the spectrum taken with a 3" NaI(Tl) detector consists mainly of the 0.51 MeV and 1.16 MeV peaks, the 1.67 MeV sum peak, and the lower energy Ti^{44} peaks. Use of a well crystal, as in Figure XI, allows one to also measure the sum peaks at 1.02 and 2.18 MeV.

Detection of Ti^{44} - Sc^{44} with a Ge(Li) diode proves to be a very selective method, as can be seen from Figure XIIA. A diode with 3 kev resolution can easily resolve the Ti^{44} gamma peaks at 68 and 78 kev. Ge(Li) - NaI(Tl) coincidence techniques could be used to resolve Ti^{44} - Sc^{44} from interfering radionuclides. Some of the diodes commercially available for low-energy (< 100 kev) measurements would be suitable for detecting the 68 and 78 kev Ti^{44} gamma rays.

In Table XIII, the detection capabilities of a number of counting systems for Ti^{44} - Sc^{44} have been compared. For purposes of this table, counting efficiency "E" is considered as the net counting rate "N" under the peak(s) of interest divided by the disintegration rate of the source. Background "B" is the background counting rate in cpm under the same peak(s). The minimum detectable activity "D" is given by the expression:

$$D = \frac{1}{E} \frac{(1 + 2C\ TB)}{C^2 T}$$

where "C" is the coefficient of variation (C = σ/N), and "T" is the total counting time, sample plus background.[146] L. Currie has recently presented another informative discussion of radiochemical statistics.[143]

FIGURE X

Spectrum of
48-Year Ti^{44}
3" x 4" NaI
Source Distance 0.5 cm
Energy Scale 10 KeV/PHU

FIGURE XI

Spectrum of
48 Year Ti^{44}

5" x 5" NaI Well Detector
Well Dimensions 1" x 3"
Energy Scale 10 KeV/PHU
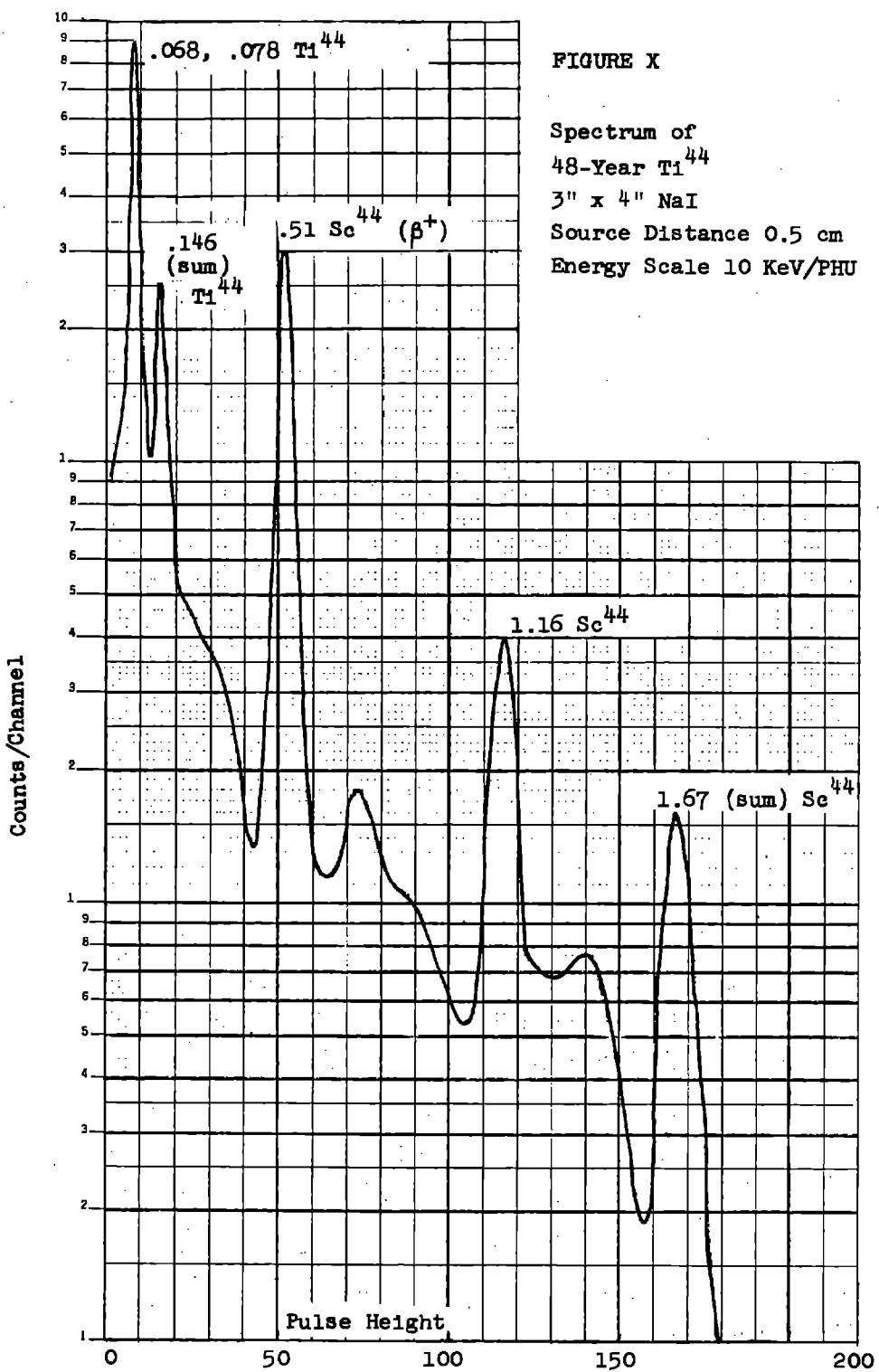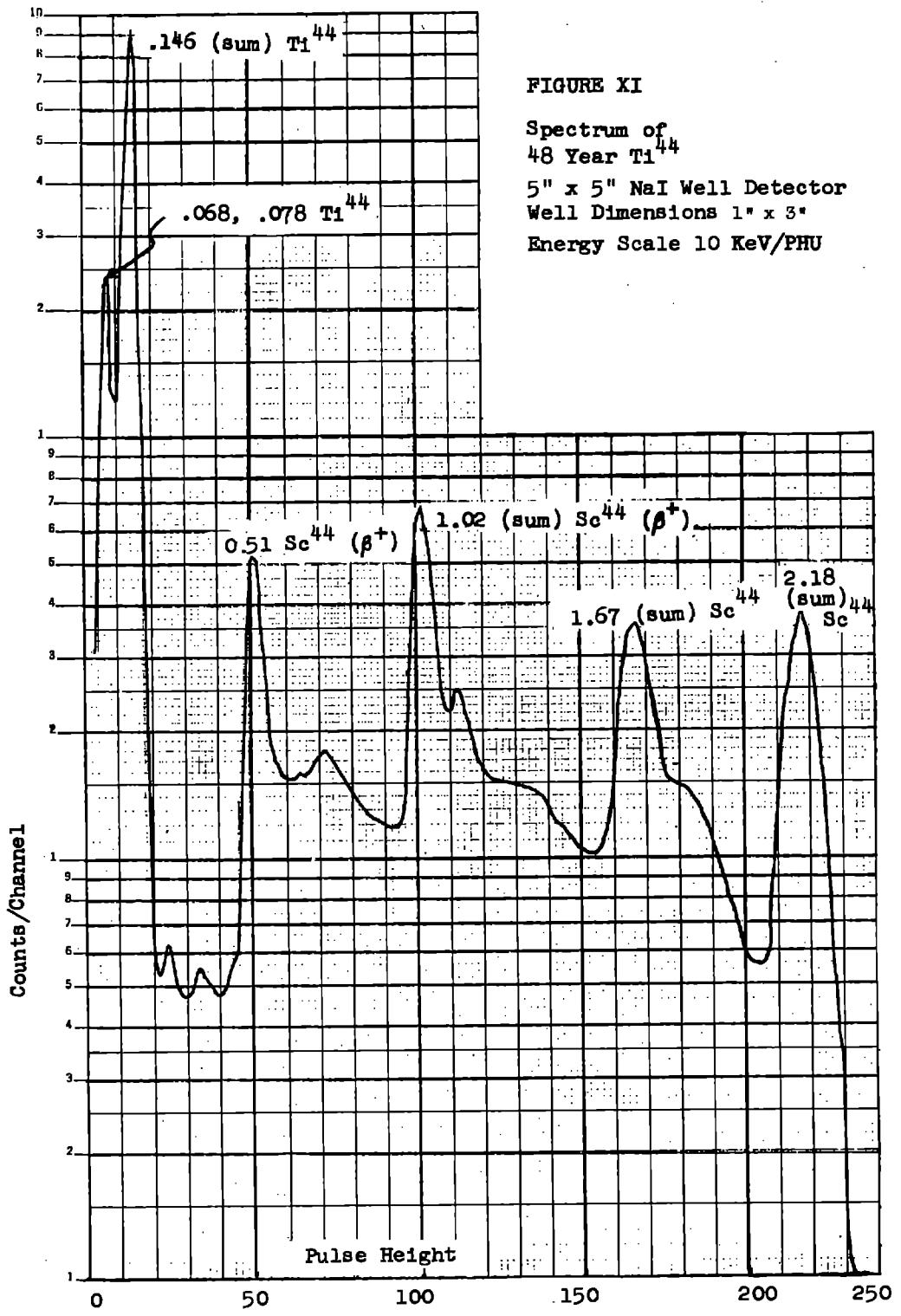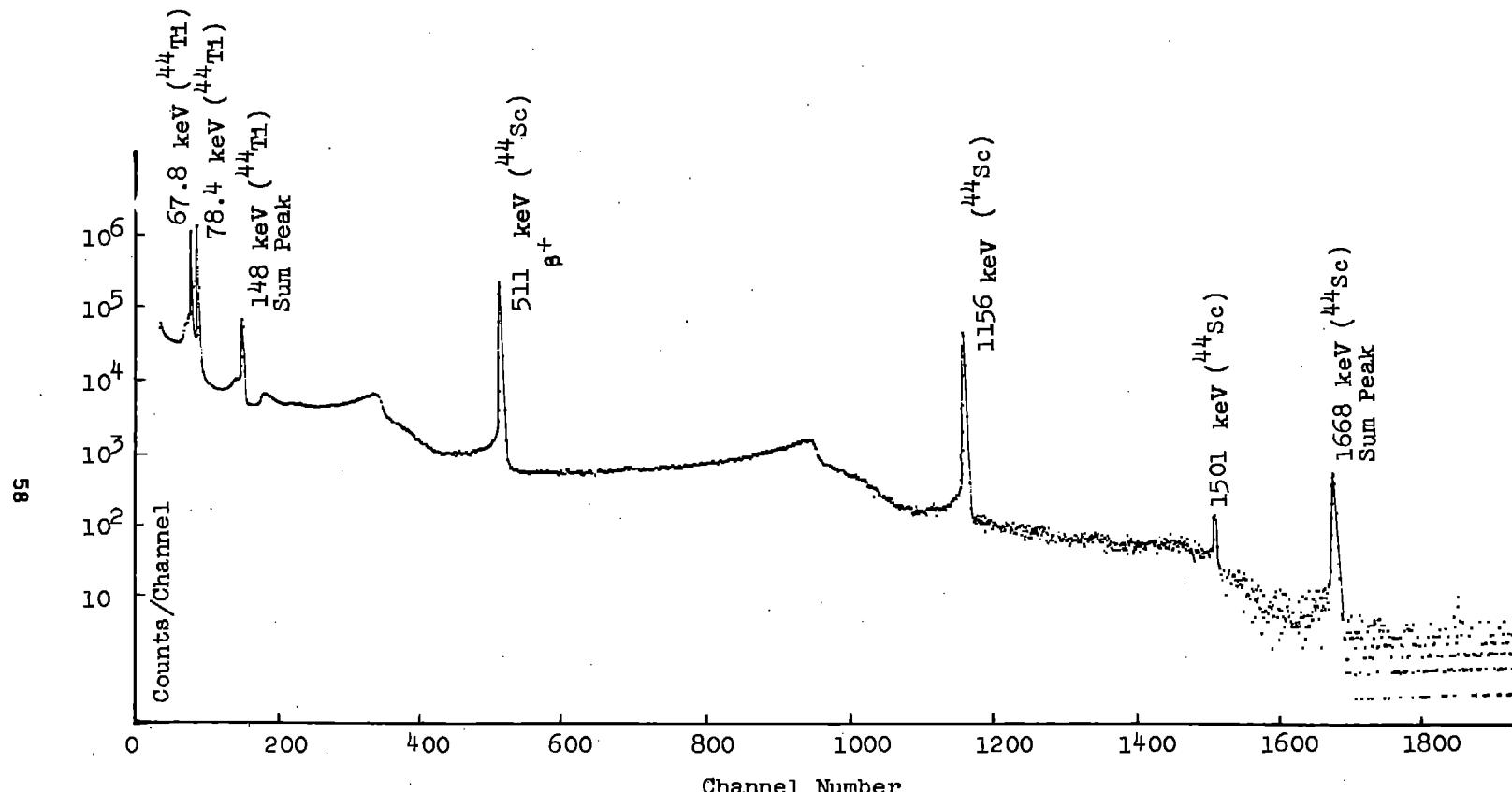
FIGURE XII A

Ge(Li) DIODE SPECTRUM OF ^{44}Ti-^{44}Sc

30 cm^3 Ge(Li) Diode
    (coaxial)
Sample 5 ml aqueous solution
    9-16-69
Energy Scale 1.0 kev/channel

Table XIII

Detection Sensitivity for Titanium-44 by Gamma Spectrometry

Detector NaI(Tl)	Mode	Peak (MeV)	Detector Efficiency	Background CPM	D_{1000}
2"x1/32"		.069, .078	.253	4.22	.367
2"x1/32" (2)	Multiparameter	.147 sum	.0338	.005	.246
3"x4"		.069, .078	.373	21.7	1.12
		.147 sum	.145	25.0	3.16
		.51	.218	21.8	1.93
		1.16	.0462	7.74	5.42
		1.67 sum	.0188	2.74	7.98
3"x4" (2)	Summed	.147 sum	.404	54.8	1.64
		1.02 sum	.0794	11.4	3.83
		1.16	.0770	18.4	5.02
		1.67 sum	.0294	6.05	7.54
		2.18 sum	.0172	3.61	10.0
	Coincidence	.147 sum	.202	.240	.227
		1.02 sum	.0823	1.17	1.20
		1.67 sum	.0213	.860	3.99
		2.18 sum	.0175	.730	4.48
5"x6" (2)	Summed	1.02, 1.16	.0899	18.0	4.25
	Coincidence	2.18 sum	.0872	1.16	1.13
	Multiparameter	2.18 sum	.0719	.218	.609
5"x5" well		.147 sum	.681	65.4	1.07
		1.02 sum	.116	13.9	2.88
		1.67 sum	.0959	8.74	2.79
		2.18 sum	.101	5.13	2.04
11"x6" (2)	Summed	1.02, 1.16	.403	487	4.90
	Coincidence	2.18 sum	.402	12.0	.776
	Multiparameter	2.18 sum	.244	.990	.373

For low-level counting, sample and background counting periods should be equal, so for a 1000 minute sample count, with a 2σ detection limit "D" becomes:

$$D_{1000} = \frac{1 + \sqrt{2000B}}{500E} \quad \text{dpm}$$

For further information on gamma spectrometry techniques the reader is referred to O'Kelley,[147] Siegbahn,[148] and Watt and Ramsden.[146]

B. Beta Counting

The 1.47, 1.37, and 0.99 MeV positrons resulting from decay of the Sc^{44} daughter in 93% of the transitions provide a sensitive means for the detection of small quantities of titanium-44. The sample must be free of beta contamination, which usually involves performing specific titanium separation and purification chemistry. After allowing sufficient time for growth of the 4.0 hour Sc^{44} daughter following final purification, the sample is counted with a geiger or proportional counter. Detection limits are determined by the amount of sample, counter background, length of counting time, and counter sensitivity, as well as the contamination limits determined by the analyst for blanks. A low-level beta system employing cosmic-ray guard detectors, mercury and lead shielding, and a small geiger counter (5 cm^2 sample area) can yield a background of 0.2 cpm, and a 2 sigma Sc^{44} detection limit of 0.105 dpm for 1000 minutes of counting.

A method which is less dependent on low blanks involves milking Sc^{44} from the parent Ti^{44} after establishing equilibrium, and following the 4.0 hour decay.

C. Other Methods

A 3.03 keV X-ray results from the electron capture decay of titanium-44; however, the low energy and low fluorescence yield of this X-ray make detection difficult. Therefore, counting methods based on X-ray detection would seem of little practical importance.

60

More exotic systems for titanium-44 measurement include beta-gamma or beta-gamma-gamma coincidence techniques, and multiparameter analysis with, or without, beta coincidence gating. Figure XIIB shows a multiparameter anticoincidence spectrum of the 2.18 MeV sum peak of titanium-44 and scandium-44 using a NaI(Tl) detector.

2. TITANIUM-45

Since titanium-45 decays to the ground state of stable scandium-45, only the positron annihilation gamma rays, shown in Figure XIII, are detectable in a NaI(Tl) detector. Discrimination from interfering radionuclides depends upon resolving the 3.08 hour half-life component at 0.51 or 1.02 MeV. The 1.02 MeV positron may also be detected with a geiger or proportional counter. Figure XIV shows the titanium-45 spectrum as measured with a Ge(Li) detector system.[149] Titanium-45 for tracer applications can be made from a (d, 2n) reaction on a scandium target. Titanium containing titanium-45 can also be produced by the titanium-46 (n,2n) reaction, and after purification of titanium and decay of titanium-51 the sample should give a relatively clean spectrum of titanium-45.

3. TITANIUM-51

Titanium-51 is most easily identified by a 0.323 MeV gamma ray resulting from the decay to stable vanadium-51. The 0.323 MeV gamma is in coincidence with a 0.61 MeV gamma during 1.4% of the transitions.[2] A 0.93 MeV gamma, although of low intensity (4.8% of decay events), may help to identify titanium-51 in the presence of interfering gammas at lower energies. A titanium-51 spectrum taken with a 3" dia. x 3" thick NaI(Tl) detector is shown in Figure XV. Kim[141] reported a counting efficiency of 20-22% for 10 ml of sample in a 3/4" x 6" test tube in a standard 1-3/4" x 2" scintillator well crystal. The beta rays of titanium-51(2.1 MeV, 94.5%; 1.5 MeV, 4.5%) can be counted in a Geiger or proportional counter, and the relatively high energy beta ray at 2.1 MeV minimizes self-absorption problems. A
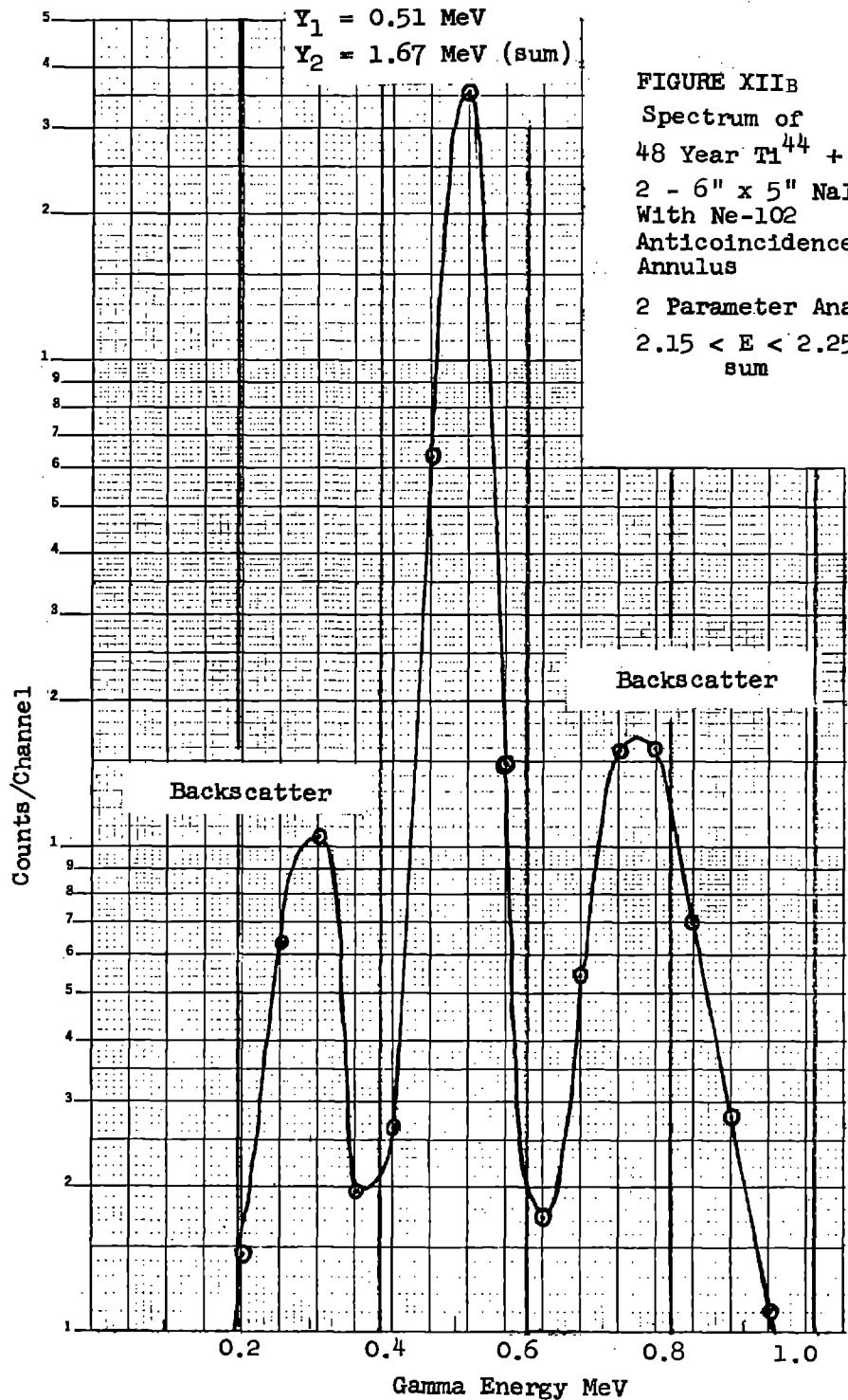
FIGURE XIIB

Spectrum of

48 Year Ti^{44} + Sc^{44}

2 - 6" x 5" NaI
With Ne-102
Anticoincidence
Annulus

2 Parameter Analysis:

2.15 < E < 2.25 MeV
     sum

Y_1 = 0.51 MeV

Y_2 = 1.67 MeV (sum)

Backscatter

Backscatter

Counts/Channel

Gamma Energy MeV

FIGURE XIII

Spectrum of
3.08 hr. Ti^{45}
3" x 3" NaI (Tl)
Absorber 1.18 g/cm^2 Be
+ 200 mg Cu Sandwich
Source Dist. 10 cm
Energy Scale 1 keV/PHU

Counts/Channel

0.51

X10

Bremsstrahlung
1.02 MeV β^+

Sum
0.51 + Backscatter

Gamma Energy MeV

0   200   400   600   800   1000

The figure contains the following labels and annotations:

- Y-axis: Counts/Channel, with gridline markers 10^6, 10^5, 10^4, 10^3, 10^2, 10, 1
- X-axis: Channel Number, with markers 0, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000

Inset text box:
- 3.08-hr Ti^{45}
- 2.5 cm^2 Area x 4mm Ge(LI)
- ABSORBER: 0.5g/cm^2 Poly
- SOURCE DIST: 3cm
- ENERGY SCALE: 1.043 keV/Channel

Annotation:
- Annihilation Radiation 511.006 keV

FIGURE XIV

Diode Spectrum of Titanium-45.   Reference 149.

FIGURE XV

Gamma Ray Spectrum of Ti[51]. Reference 141.
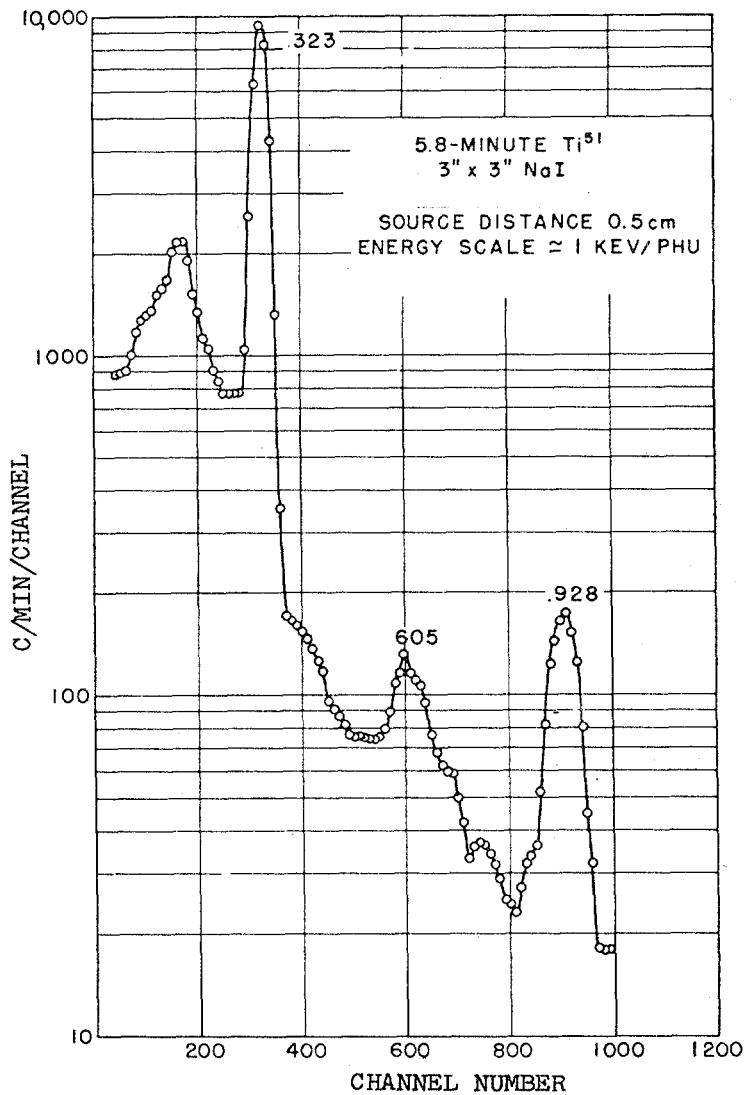
photopeak efficiency of 23% would be expected for the 0.323 MeV gamma from a point source at a distance of 0.6 cm from a 3" x 3" NaI(Tl) crystal.[150]

VII. Radiochemical Separation Procedures

The first five procedures are applicable to the five-minute isotope titanium-51 and the three-hour isotope titanium-45. The next two procedures are quite time consuming, and may be applicable to titanium-44 studies in geochemical samples and meteorites. Procedures 8 and 9 are included as means of milking the scandium-44 daughter from the parent titanium-44.

The scarcity of radiochemical procedures for titanium has been mainly due to the lack of a suitable isotope for tracer studies until recently, and the fact that titanium isotopes are not important in fission of uranium and plutonium. It is encouraging that high energy nuclear physics and spallation studies are contributing to this subject.

Preparation of Titanium Carrier

(1) $K_2TiF_6 \cdot H_2O$ Method

Weigh approximately 13.5 g of $K_2TiF_6 \cdot H_2O$, transfer to a Pt dish, and treat with 50 ml 1:1 H_2SO_4. Evaporate to fumes of SO_3, cool, add 10 ml H_2O, evaporate again to fumes of SO_3. Cool, dilute to 250 ml. Remove aliquots for analysis.

(2) $TiCl_3$ Method

Transfer 40 ml reagent grade $TiCl_3$ (20%) to a beaker. Add a few ml 1M HCl and sufficient H_2O_2 to give an orange color. Boil until orange color disappears, then dilute to 250 ml with 1 M HCl. Remove aliquots for analysis.

(3) TiO_2 Method

Place 1.0 g analytical grade TiO_2 in a crucible. Add about 8 grams ammonium bisulfate, mix, then cover the top of the mixture

with ammonium bisulfate. Partially cover the crucible and heat

gently to avoid spattering until the mixture is molten. Swirl

mixture, and heat until all TiO_2 is dissolved in the

melt. Cool, and dissolve melt in 1 M HCl (or H_2SO_4). Filter

any residue. Dilute filtrate to 250 ml with 1 M HCl and remove

aliquots for analysis.

Analysis of Aliquots

Dilute aliquot to 100 ml, then make just basic with NH_4OH.

Boil 5 minutes, filter, and wash the precipitate with distilled

water. Ignite in a crucible to TiO_2, cool, and weigh. Calculate

Ti content in mg Ti per ml of carrier solution.

Note: Alternatively, Ti may be determined in the aliquots by

spectrophotometry of the Ti(IV) peroxo complex.

PROCEDURE 1

Source - C. K. Kim, University of Michigan[141]

Element separated: Titanium   Time for sep'n: 13 minutes

Target material: Meteorites, rocks and   Equipment required: 30 ml
    minerals, alloys, botanical and   nickel crucible with a
    biological ashes.   lid, Fisher burner,
                                                    centrifuge, separatory
Type of bbdt: Neutron activation;   funnel.
    15 minute irradiation at 10^{12} n
    cm^{-2} sec^{-1}

Yield: ~ 68%

Degree of purification: Slight contamination of Mn^{56} and V^{51}.

Procedure:

(1) Heat 5 ml Ti^{+4} carrier (0.8 mg) in nickel crucible to dryness; add

4 or 5 g Na_2O_2. (The amount of carrier added is dependent on the

titanium content in the sample).

(2) Add ~ 0.1 g of irradiated finely ground sample and put on lid tightly

(note a); fuse for one minute; swirl melt onto side of crucible. Cool

67

crucible and contents rapidly by dipping base of crucible into cold
water until the contents have solidified.

(3) Dissolve the solidified melt in H_2O, boil, centrifuge and acidify
the residue with either HCl or H_2SO_4.

(4) Add Fe carrier and make the solution alkaline with NH_4OH to preci-
pitate TiO_2; centrifuge.

(5) Add 20 ml of 10% H_2SO_4 to the residue and add 10 ml of 6% aqueous
cupferron and 10 ml of isopropyl ether. Shake vigorously. Ti^{+4} extracts
into the organic layer. Draw off the aqueous layer (crushed ice should
be used to keep the liquids cool).

(6) Add crushed ice to the ether solution; back wash with 20 ml of
cooled 15% NaOH (Cu, V, Mo, W are eliminated here).

(7) Wash ether fraction with 10% H_2SO_4 and transfer ether to marked
tube for counting.

(8) Count 0.32 Mev γ-ray of 5.8-minute Ti^{51} with γ-spectrometer;
determine chemical yield by measuring (after decay) the pertitanic
acid (yellow) with a Beckman Spectrophotometer (420 mμ).

Notes:

a) If the sample is irradiated in a gelatin capsule and the capsule
is also fused, care must be exercised because the gelatin capsule is
vigorously attacked by the peroxide.

b) Depending on the type of sample, some of the steps in the separation
could be omitted. For instance, unless a large amount of vanadium is
contained in the sample, step 6 (NaOH backwashing) is unnecessary
since most of the vanadium is eliminated as the sodium vanadate which
is dissolved in water when the Na_2O_2 melt is treated with water and
centrifuged. However, if there is a large amount of vanadium in the
sample, a trace of vanadium might come down with titanium and it
interferes with the spectrometrical determination of titanium.
Although NaOH backwashing eliminates vanadium very well, at the same

68

time it reduces the chemical recovery of titanium appreciably by forming a titanium oxide precipitate.

c) The temperature should be kept low (~ 10° C) preceding the NaOH backwashing and the aqueous layer should be removed immediately after the shaking. A filtering step through a fine sintered glass chimney or Whatman No. 42 filter paper is required if a large amount of sample is fused because an insufficient fusion time may result in incomplete fusion.

d) Step 4 is not necessary except if a fair amount of copper is present in the sample. Copper is a rather serious contamination if it comes down with titanium since it has a 0.511 Mev annihilation peak near to the 0.32 Mev titanium peak. Step 6 also eliminates copper.

e) Step 7 should be done twice if possible to eliminate mechanical contamination which always accompanies solvent extraction. Care must be taken to draw the aqueous layer completely from the ether layer. Throughout the experiment, it is necessary to keep the temperature rather low (~ 10° C) so as not to destroy the cupferron. Often, the heat involved in the neutralization with NaOH will cause trouble.

f) If 0.3-0.4 mg of titanium is contained in the sample, either a large amount of Ti carrier or a small amount of the sample should be taken so that the colorimetric yield determination gives reproducible values. For a large amount of titanium carrier, 500 mμ should be used instead of the normal 420 mμ photometric determination.

g) Much practice will be required for the Na_2O_2 fusion. A ring clamp for holding the nickel crucible should be one inch away from the surfaces of the burner for best results. When the crucible becomes red, a swirling motion is recommended. Air cooling from red crucible to black makes it easy to dissolve the melt with water.

h) In its simplest form of one cupferron extraction and a double H_2SO_4 wash, this procedure can be completed in 8 minutes on a sample such as aluminum alloy with a yield of around 92%.

69

PROCEDURE 2

Source - C. K. Kim, University of Michigan[141]

Element separated: Titanium   Time for sep'n: ~ 10 min.

Target material: Meteorites, rocks and   Equipment required:
        minerals; biological and   Standard plus 30 ml
        botanical samples   nickel crucible and
                                                     sintered glass filter
Type of bbdt: Neutron activation   with chimney.

Yield: ~ 85%

Degree of purification: Good for gamma spectroscopy

Advantages: Fast and simple

Procedure:

(1) Heat 5 ml Ti^{+4} carrier (0.8 mg) in nickel crucible to dryness; add 4 or 5 g Na_2O_2. (The amount of carrier added is dependent on the titanium content in the sample).

(2) Fuse ~ 0.1 g of irradiated finely ground sample for one minute; swirl melt onto side of crucible. Cool crucible and contents rapidly by dipping base of crucible into cold water until the contents have solidified.

(3) Dissolve the melt in H_2O and centrifuge.

(4) Dissolve the residue in a minimum of concentrated H_2SO_4. Dilute this solution to 2 N in H_2SO_4 and filter.

(5) Add Zr carrier and boil the solution. Add 4% p-hydroxyphenylarsonic acid in moderate excess and stir vigorously.

(6) Digest over a hot plate.

(7) Cool moderately and filter through Whatman No. 42 filter paper on the sintered glass filter.

(8) Transfer the precipitate to a teflon covered counting card and count the 0.32 Mev γ-ray of Ti^{51} with γ-spectrometer; determine chemical yield by dissolution and measuring pertitanic acid (yellow) with Beckman Spectrophotometer (420 mμ)[61]

Notes:

For a sample abundant in chromium, an anion exchange column should be used to adsorb chromate ions prior to step 5.

PROCEDURE 3

Source - C. K. Kim, University of Michigan[141]

Element separated: Titanium   Time for Sep'n: ~ 11 min.

Target material: Aluminum alloy   Equipment required:

Type of bbdt: Neutron activation   Standard

Yield: 5 - 85%

Degree of Purification: Fairly good (Mn^{56} contaminated)

Advantages: Rapid separation

Procedure:

(1) Dissolve the irradiated sample in concentrated HCl with 5 ml of Ti carrier (~ .8 mg Ti). Heat, add Cu carrier and dilute with water until weakly acidic.

(2) Pass H_2S gas through the solution to precipitate the sulfides of contaminants (particularly Cu if present); boil the solution, centrifuge and filter.

(3) Add Fe carrier to the filtrate, add Na_2O_2 powder until it becomes alkaline, boil, and centrifuge.

(4) Dissolve residue in 10% H_2SO_4. Cool. Extract Ti^{+4} with 10 ml of 6% cupferron in isopropyl ether.

(5) Wash the ether extractant with 10% H_2SO_4 twice and draw off the aqueous layer.

(6) Evaporate the ether in a 150 ml beaker over a hot plate.

(7) Position the 150 ml beaker in front of the NaI crystal and count the 0.32 Mev γ-ray from Ti^{51} by γ-spectrometry. Determine the chemical yield by dissolving the residue in the beaker and measuring pertitanic acid (yellow) with Beckman spectrophotometer (420 mμ).[61]

71

Note:

The counting of the residue on the bottom of the beaker (step 7)

increases the counting efficiency about three times over the counting

of a liquid sample.

PROCEDURE 4

Source - C. K. Kim, University of Michigan[141]

Element separated: Titanium   Time for sep'n: 12 minutes

Target material: Botanical and   Equipment required: Standard
        biological samples

Type of bbdt: Neutron activation

Yield: 90%

Degree of purification: Fairly good for γ-spectrometry

Advantages: Fast and simple

Procedure:

(1) Leach the sample with concentrated HNO_3 and heat to dryness in a

250 ml beaker. Add 72% $HClO_4$ and fume.

(2) Add concentrated HCl and clarify solution by heating.

(3) Add Fe carrier and make the solution alkaline with NaOH to pre-

cipitate $Fe(OH)_3$ and TiO_2. Centrifuge.

(4) Dissolve the residue with 10% H_2SO_4. Cool.

(5) Extract Ti^{+4} with 10 ml 6% cupferron in 10 ml isopropyl ether.

(6) Wash the ether extractant with 10% H_2SO_4 twice and draw off the

aqueous layer.

(7) Transfer the ether layer to a counting tube and count the 0.32

Mev γ-ray of 5.8-minute Ti^{51} by γ-spectrometry. Determine the chemical

yield by measuring pertitanic acid (yellow) with Beckman spectrophotometer

(420 mμ).[61]

Notes:

a) Step 3 can be eliminated if the sample does not contain a large

amount of any one element. Iodine is a rather significant problem, however,

72

in handling marine organisms; Fe does not carry iodine down with the titanium. A preliminary CCl_4 extraction can be used to eliminate much of the iodine if desired, but it must be repeated at least twice for this purpose. Fuming with concentrated H_2SO_4 expels most of the iodine; however it is not advisable to use this technique because active iodine might contaminate the hood. $Na_2S_2O_3$ absorbs iodine upon filtering the solution but a trace amount is still retained in the solution.

b) Fusion with $Na_2S_2O_7$, $NaHSO_3$, or KHF_2 in platinum crucible can be substituted for the acid leach in step 1. The melt is then dissolved in concentrated H_2SO_4 and water. Silica rocks can be fused with HF plus H_2SO_4 in a platinum crucible. If a large amount of vanadium is a contaminant in a sample, 15% NaOH backwashing should be done after the cupferron extraction in place of step 3.

PROCEDURE 5

Source - C. K. Kim, University of Michigan[141]

Element separated: Titanium   Time for sep'n: 17-20 minutes

Target material: NBS Ferrochromium   Equipment required: Standard
    alloy containing 0.034% Ti.   plus 30 ml nickel crucible
                                 with lid, separatory funnel.

Type of bbdt: Neutron activation

Yield: ~ 50%

Degree of purification: Some Cr^{51}, Mn^{54}, and V^{52} contamination.

Disadvantage: Procedure takes too long for 5.8-minute half-life.

Procedure:

(1) Fuse the irradiated sample with Na_2O_2 in a nickel crucible; swirl the melt onto side of crucible. Cool crucible and contents rapidly by dipping base of crucible into cold water until contents have solidified.

(2) Dissolve the melt in water, centrifuge, and acidify with concentrated H_2SO_4.

(3) Add NH_4OH to precipitate TiO_2, centrifuge and dissolve the residue in 1 N HCl.

73

(4) Add Zr carrier and precipitate the Titanium(IV) with p-hydroxypehnylarsonic acid; stir vigorously and centrifuge.

(5) Dissolve the precipitate with 15 ml of 7 M H_2SO_4.

(6) Extract Ti^{+4} with 4% tri-octylphosphine oxide (TOPO) in hexane by shaking or stirring with a glass rod mechanically for 10 minutes.

(7) Draw off hexane phase and transfer extractant to counting tube for counting. Count the 0.32 Mev γ-ray of 5.8-minute Ti^{51} with γ-spectrometry.

Notes:

a) The chemical recovery is proportional to the length of stirring time in the TOPO extraction. TOPO extraction for various elements has been thoroughly studied by White.[151]

b) An oxine extraction combined with EDTA-masking could be used in place of the TOPO extraction. However, oxine is selective only at a specific pH and it takes time to adjust to a pH of 5-7 (the range in which titanium is extracted). Besides, titanium tends to hydrolyze at a pH of 5-7 to give a white precipitate. Therefore, tartaric acid should be used for the separation. The separation requires about 15 minutes, gives poor recovery of Ti and furthermore gives contamination of V, Mn, and others.

(3) The cupferron extraction appears to be much better for Ti than the above two extractants.

PROCEDURE 6

Source - M. T. Lipschutz, University of Chicago

Element separated: Titanium   Time for sep'n: days

Sample material: Iron meteorites
                  60-190 grams

Degree of purification: Separates Ti from cosmogenic and natural
                         radionuclides encountered in meteorites.

Advantages: Good separation of Ti^{44} for gamma coincidence analysis.

Procedure:

(1) Reflux sample in conc. HCl+HNO$_3$. Magnetic particles still present in residue may be treated with HNO$_3$ and this solution is then added to the main solution. Add 50 mg. Ti^{+4} carrier, and carriers for other elements of interest.

(2) Convert solution to 8 M HCl, and extract iron into isopropyl ether.

(3) Evaporate HCl layer, convert to a 1 N H$_2$SO$_4$ solution of 1-2 liter volume.

(4) Electrolyze solution with a mercury cathode at 10-20 amps and 3.4 volts until loss of color indicates removal of Ni^{+2} and Co^{+2}.

(5) Concentrate solution to 1.8 N H$_2$SO$_4$, and precipitate titanium by addition of 4% p-hydroxyphenylarsonic acid solution. Ignite precipitate to TiO$_2$ and fume to dryness with HF solution to volatilize silicon as SiF$_4$. Ignite again, and determine titanium yield gravimetrically as TiO$_2$. Mount for gamma counting and allow Sc^{44} to grow in. No chemical yield correction is usually necessary for titanium from iron meteorites.

PROCEDURE 7

Source - P. J. Cressy, Goddard Spaceflight Center, Greenbelt, Maryland

J. H. Kaye, Battelle-Northwest, Richland, Washington

Element separated: Titanium   Time for sep'n: days

Sample material: stone meteorites 150-400 grams
                 iron meteorites 150-400 grams

Yield: 53-87%

Degree of purification: Separates Ti from cosmogenic and natural
                        radionuclides encountered in meteorites.

Advantages: Ti^{44} may be estimated by gamma analysis or Sc^{44} may
            be milked from the purified Ti for beta counting.
            Procedure includes spectrophotometric analysis of Ti
            in stone meteorites.

Procedure:

A. Dissolution of Stone Meteorites and Separation of Iron

(1) Clean specimen with acetone, grind in agate mortar to powder, and weigh. Add 400 ml 48% HF. After reaction subsides, add 100 ml conc. H_2SO_4. Heat mixture until silicon is expelled.

(2) Transfer to teflon evaporating dish, add 200 ml conc. H_2SO_4, and evaporate under heat lamp until dry. Add 200 ml conc. HNO_3, evaporate, repeat twice.

(3) Transfer to a 2-liter porcelain evaporating dish, add 400 ml conc. HCl, and evaporate to dryness. Repeat twice with 200 ml portions conc. HCl. Dissolve residue in 9 M HCl.

(4) Prepare three 2-liter separatory funnels, each containing 400 ml isopropyl ether saturated with 9 M HCl. Add meteorite solution and extract iron by counter-current method. Wash combined ether layers twice with 100 ml of 9 M HCl, and combine washings with main HCl solution. Skip to step C5.

B. Dissolution of Iron Meteorites and Separation of Iron

(1) Wash sample with acetone, then etch with 8 M HNO_3, rinse with distilled water, and weigh.

(2) Decompose by addition of 8 M HNO_3 dropwise (into a reaction vessel fitted with traps to capture volatile gases if C^{14}, Cl^{36} are to be determined). After reaction slows, heat to ensure dissolution.

(3) Add carriers for Ti(IV) (100 mg TiO_2 equivalent), and other elements of interest. Filter solution. Remove Cl^- if Cl^{36} is to be measured by adding 2% $AgNO_3$ and filtering or centrifuging the resulting AgCl precipitate.

(4) Evaporate solution, convert to 3M HCl. After allowing solution to stand for several hours, filter any silica present and AgCl if excess Ag^+ was added in step 3. Evaporate filtrate, convert to 9 M HCl, and remove iron by counter-current solvent

76

extraction using 4-500 ml portions of isopropyl ether pre-equili-
brated with 9 M HCl. Back-wash the ether layer twice with 9 M
HCl and combine washings with main HCl layer.

C. Separation and Purification of Titanium

(5) Heat 9 M HCl solution briefly to drive off ether. Pass
through an anion exchange column containing 250 ml wet volume of
Dowex 1 X-8 (50-100 mesh) resin, which has been washed with four
column volumes of distilled water and of 9 M HCl. Elute
meteorite with 9 M HCl solution at 2-3 ml per minute.

(6) Evaporate the 9 M eluent to a small volume, and cool to below
5°C. Add 30 ml chilled 6% aqueous cupferron solution. Extract
yellow titanium cupferron complex into 250 ml chloroform.
Repeat extraction 2-3 times. Combine chloroform layers, wash
with cold 6 M HCl.

(7) Evaporate almost to dryness. Add conc HNO_3 cautiously and
heat to destroy organic matter. Repeat. Add 20 ml conc H_2SO_4
and heat until clear or pale yellow. Dilute to 100 ml with 0.3 M
H_2SO_4. Add 5 g of tartaric acid and 10 mg of Cu^{+2} carrier.

(8) Precipitate CuS with H_2S, filter and discard the precipitate.
Boil the filtrate, then neutralize with NH_4OH. Filter any preci-
pitate and discard. Evaporate filtrate, and destroy organic
material (cautiously!) with conc HNO_3. Dissolve final residue
in 0.3 M H_2SO_4.

(9) Add 5 ml of 30% EDTA solution, adjust to pH 5.0 with NH_4OH,
and cool to below 5°C. Add 30 ml cold 6% cupferron, let stand
15 minutes in ice. Filter on Whatman 40 paper, wash with cold 1%
cupferron solution, ignite to TiO_2, weigh.

Note: Sc^{44} may be milked from the purified TiO_2, after allowing
for growth to equilibrium, using procedure 8.

D. Estimation of chemical yield of titanium (source: P. J. Cressy)

   (1) An aliquot from the meteorite solution after dissolution, containing about 0.5 mg titanium, is taken for analysis (step A3). (Note: stone meteorites contain .08-.15 % TiO_2 by mass). Evaporate with H_2SO_4 to SO_3 fumes.

   (2) Dissolve residue in 2 M H_2SO_4, dilute to 100 ml. Two 10-ml and two 20-ml aliquots are taken for analysis.

   (3) Add ten drops 30% H_2O_2 to one aliquot of each volume, using the remaining aliquots for reference. The absorption spectrum from 350-650 millimicrons is taken for each set of aliquots.

   (4) The transmittance of each sample at 420, 430, 440, 450, and 460 millimicrons is determined. The weight of titanium corresponding to the transmittance at each wavelength is obtained from the standard extinction plots. The five values for each set of aliquots are averaged, and the two resulting mean titanium contents are averaged.

Note:

The standard extinction plots are obtained by making up a synthetic meteorite solution with varying amounts of titanium, and measuring the transmittance vs. titanium content.

PROCEDURE 8

Source - J. H. Kaye, Battelle-Northwest, Richland, Washington

Element separated: Scandium   Time for separation: less
                                                             than 4 hours

Sample material: Titanium dioxide

Yield: 90%

Degree of purification: Separates Sc^{44} from any beta impurities
                        present in TiO_2 from procedure 7.

Advantages: Sc^{44} may be determined by following the 4.0 hour decay,
            either by gamma or beta counting.

Procedure:

(1) Fuse TiO$_2$ with sodium bisulfate, dissolve in 3 M HCl. Add 20 mg Sc^{+3} carrier. Extract TiO$_2$ into 100 ml CHCl$_3$ using 20 ml cold 6% aqueous cupferron, and repeat.

(2) Wash aqueous layer twice with CHCl$_3$. Add NH$_4$OH to precipitate Sc(OH)$_3$. Centrifuge, wash with 20 ml distilled water.

(3) Pass sample through a 10-ml Dowex 50, X-8 (100-200 mesh) cation exchange column. Wash with 25 ml 2 M HCl. Elute Sc^{+3} with 50 ml 6M HCl. Evaporate 6 M eluent, precipitate Sc(OH)$_3$ with NH$_4$OH. Filter, wash with distilled water, and ignite to Sc$_2$O$_3$. Weigh, mount, and count by following the 4.0 hour β^+ decay. Correct decay to time of cupferron extraction.

Note:

Commercial Sc$_2$O$_3$ often contains beta impurities. For low-level Sc^{44} measurements it may be helpful to purify the Sc carrier before adding to the sample.

PROCEDURE 9

Source: M. W. Greene and M. Hillman, Brookhaven National Laboratories.[152]

Isotope Separated: Scandium-44

Sample Material: Titanium-44 "Cow"

Yield: 60 - 70%

Degree of Purity: ca. 0.02% contamination

Advantages: A convenient source of easily detected, short lived scandium-44.

Procedure:

(1) A column of 10-15 ml of Dowex-1, X-8 (50-100 mesh) anion exchange resin in the chlorine form was prepared. A 2 cm tube with a coarse frit as base was recommended as a column. A 0.5 cm layer of powdered quartz between two discs of filter cloth was held in place at the top of the resin bed by a split polyethylene ring. This layer prevented

79

mixing of the resin and also prevented draining of the column which must not become dry.

(2) The column was rinsed free of excess chloride with water.

(3) One to two drops of 3% H_2O_2 was added to each ml of titanium-44 solution. The product was evaporated to dryness and then taken up in 20 ml of 0.1 M oxalic acid.

(4) The titanium-44 oxalate solution was loaded on the resin and washed with 40 ml of a solution which was 0.1 M in oxalic acid and 0.2 M in HCl.

(5) The generator is milked by eluting with 30 - 50 ml of the 0.1 M oxalic - 0.2 M HCl solution.

(6) Long lived contamination increases with use but can be reduced again by eluting the titanium-44 from the column with 1 M HCl. The titanium-44 is then reloaded as in steps 3 and 4.

PROCEDURE 10

Source - Gösta Rudstam, Forskningsrådens Laboratorium, Nyköping, Sweden[153]

Element separated: Titanium   Purpose: To remove other spallation

Target Material: Cobalt   products from Cobalt

Type of bombardment: 170-Mev Protons   Time for Separation: 60 min.

Yield: 10 - 50%   Volumes: Less than 10 ml.

PROCEDURE:

(1) The targets were dissolved in dilute nitric acid containing 0.2 mg of titanium carrier together with iron and vanadium carriers.

(2) The solution was made ammoniacal, and the resulting precipitate was washed twice with dilute ammonia.

(3) The washed precipitate was boiled with 1 M NaOH containing H_2O_2.

(4) The precipitate was then dissolved in HCl and more vanadium carrier, NaOH, and H_2O_2 were added. The mixture was boiled.

(5) After centrifuging, the precipitate was washed and then dissolved in 6 M HCl.

(6) All iron was removed from the resulting HCl solution by repeated extraction with diethyl ether.

(7) The aqueous phase was made 1 M in HCl and 1 ml of 6% aqueous cupferron solution was added. The titanium cupferrate was extracted into chloroform.

(8) The chloroform solution was washed twice with 1 M HCl and then evaporated and ignited into a porcelain crucible.

(9) The TiO_2 residue was dissolved in 1 M nitric acid which was evaporated to 0.5 ml to form the titanium test solution.

(10) The titanium concentration of the test solution was determined spectro-photometrically using chromotropic acid.[154]

PROCEDURE 11

Source: G. Rudstam, P. C. Stevenson, and R. L. Folger[155]

Element separated: Titanium

Target Material: Iron

Type of bombardment: 340-Mev Protons

PROCEDURE:

(1) The targets were dissolved in 12 M HCl, or sometimes, 6 M HNO_3, containing 10 mg of Ti(IV).

(2) From a 6 M HNO_3 solution of the target, titanium iodate was precipitated*. (*Procedure 12, Barr, suggests using 0.5 M KIO_3)

(3) The $Ti(IO_3)_4$ precipitate was dissolved in dilute HCl containing sufficient Na_2SO_3, or H_2SO_3, to reduce the iodate to iodine.

(4) Concentrated ammonia, or NH_3 gas, was then used to precipitate TiO_2. (NH_3 gas was preferred.)

(5) The hydrous oxide was dissolved in 10-20 ml of 0.5 M HNO_3 and the solution was scarenged with yttrium. This was done by adding 5 to 10 mg of yttrium chloride or nitrate in very dilute acid, adding 1 or 2 ml of saturated oxalic acid, stirring vigorously, and digesting in a hot water bath for several minutes. The yttrium oxalate precipate was discarded.

(6) About 1 ml of saturated tartaric acid was added to the resulting solution. The solution was made ammoniacal and 5-10 mg of iron(III) and manganes(II) chlorides were added. Sufficient tartrate prevents precipitation. The solution was then Gubbled with H_2S gas and the resulting iron and manganese sulfides were discarded.

(7) The solution from this scarenge was made 1 M in HCl and about 15 ml of cold 6% aqueous cupferron was added. Standing in an ice bath 15 minutes completed the precipitation.

(8) This precipitate was converted to hydrous titanium oxide using ammonia.

81

(9) The hydrous oxide was dissolved in 6 M HCl and the titanium again
     precipitated as the iodate.

(10) The titanium iodate was dissolved in dilute HCl and H_2SO_3 as in step (3).

(11) The final titanium hydrous oxide precipitate was made by adding ammonia
     to this solution, washing and igniting to the weighable TiO_2.

Note: This procedure was designed to separate titanium from an iron target,
       therefore, decontamination from Zr and Hf was not determined.

PROCEDURE 12

Source: Donald W. Barr[156]

Element separated: Titanium

Target material: Copper

Type of bombardment: 5.7-Bev Protons

Yield: 30%

Procedure:

(1) The copper foils were dissolved in a minimum of concentrated HNO_3
     containing the desired carriers including 5 mg of titanium as TiO_2.

(2) The solution was adjusted to 1 M in HCl and the copper was precipitated
     with H_2S.

(3) Titanium was precipitated as the hydrous oxide which was washed and
     dissolved in HCl.

(4) Tartaric acid was added to complex the titanium, and an iron-manganese
     basic sulfide scavenge was performed.

(5) The titanium containing solution was made 1 M in HCl and 6% aqueous
     cupferron was added.

(6) Titanium cupferrate was extracted into chloroform and washed with
     1 M HCl.

(7) The chloroform solution was evaporated over concentrated HNO_3 to
     eliminate any organic material.

(8) The resulting residue was dissolved in acid and made alkaline to
     precipitate TiO_2.

(9) This precipitate was dissolved in 6 M HNO_3, and 0.5 M KIO_3 was added.

(10) The titanium iodate precipitate was dissolved using HCl and Na_2SO_3.

(11) Titanium hydroxide, precipitated from this solution, was used for
     counting.

(12) Spectrophotometric analysis of this precipitate, using the peroxide
     method in sulfuric acid, was used to calculate the chemical yield.

Source: Seymour Katcoff, Brookhaven National Laboratory

Element separated: Titanium

Yield: 5-10%

Target material: Silver

Degree of Purification: good
to excellent

Type of Bombardment: High energy protons

Time for Separation: 4 hours

Procedure:

(1) Dissolve irradiated Ag target in 10 ml 4N HNO_3 containing 1 ml 27 M HF
and 20-30 mg Ti carrier in a plastic centrifuge tube (solution should
be free of $SO_4^=$ ions).

(2) Make 1 M in HCl and centrifuge off the AgCl.

(3) Add 5 mg La^{+3}, stir, and centrifuge off the LaF_3. Repeat.

(4) Precipitate $BaZrF_6$ by adding 5 mg Zr carrier, 1 ml $Ba(NO_3)_2$ solution
(50 mg/ml), and 1 ml 27 M HF. Centrifuge and repeat 3 more times.

(5) To the supernate add 10 ml saturated H_3BO_3 and excess conc. NH_4OH to
precipitate hydrous TiO_2. Allow to stand for 10 minutes and then
centrifuge. Dissolve in HCl, dilute to 15 ml. Re-precipitate TiO_2,
centrifuge, wash, and re-centrifuge.

(6) Dissolve in a minimum of saturated oxalic acid ($\sim$ 4 ml). Transfer to
a DOWEX-1, X8, anion exchange column, 100-200 mesh, 8mm diam, 16 cm
long. The column is prepared by washing with a solution 1M in HCl,
0.5 M in oxalic acid, and 0.035 M in H_2O_2. Elute the Ti with this same
solution.

(7) Precipitate hydrous TiO_2 by adding 4 M NaOH. Stir and centrifuge.
Dissolve in dilute HCl, re-precipitate, and centrifuge.

(8) Dissolve in HNO_3 and add few mg V^{+5} carrier. Precipitate $Ti(IO_3)_4$
with 20 ml of 0.5 M HIO_3 in 6 N HNO_3. Centrifuge. Dissolve by adding
10 ml 3 M HCl and solid Na_2SO_3.

(9) Precipitate TiO_2 with NH_4OH, centrifuge, and dissolve in 2 ml conc.
HNO_3. Dilute to 5 ml and precipitate $Ti(IO_3)_4$ again by adding 20 ml.
of 0.5 M HIO_3 in 6 M HNO_3. Centrifuge. Dissolve as in step 8.

(10) Precipitate TiO_2 with NH_4OH, centrifuge, and dissolve in minimum 6 N HCl.
Transfer to a small glass vial, dilute to a standard volume, and count with
a NaI well crystal.

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91

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