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The Radiochemistry of Titanium

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The Radiochemistry of Titanium

CHONG KUK KIM

Department of Chemistry
University of Michigan
Ann Arbor, Michigan

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Subcommittee on Radiochemistry
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FOREWORD

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

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

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

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

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CHONG KUK KIM[*]
Department of Chemistry
University of Michigan
Ann Arbor, Michigan

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1. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VII, Longmans, Green and Co., London, (1923), pp. 1-97.
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[*] Present address: Atomic Energy Research Institute, P. O. Box 7, Chunyang-Ni, Seoul, Korea

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF TITANIUM

1. Rodden, C. J., "Analytical Chemistry of the Manhattan Project", National Nuclear Energy Series, Vol. I, Div. VIII, McGraw-Hill Book Company, (1950), pp. 469-474.

Very little information is available on radiochemical separations of titanium.

III. TABLE OF ISOTOPES OF TITANIUM*

Isotope	Half-Life	Type of Decay	Method of Preparation
Ti^{44}	~ 10^3 yrs.	EC	Sc^{45} (p, 2n)
		0.070γ	Sc^{45} (d, 3n)
Ti^{45}	3.09 hr.	1.00 β^+ (83%)	Sc^{45} (d, 2n)
		EC (17%)	
Ti^{46}	Stable (7.99%)		
Ti^{47}	Stable (7.32%)		
Ti^{48}	Stable (73.99%)		
Ti^{49}	Stable (5.46%)		
Ti^{50}	Stable (5.25%)		
Ti^{51}	5.80 min.	2.13 β^- (94.5%)	Ti^{50} (n, γ)
		1.50 β^- (5.5%)	
		0.323 γ (96%)	
		0.93 γ (4%)	
		0.60 γ (1%)	

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* For more complete information in these isotopes and references to the original literature see "Table of Isotopes", D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Mod. Phys. 30, No. 2, Part II, 585, (1958).

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

1. Metallic Titanium

Titanium metal has a specific gravity of 4.50 (1) at 20°C, a melting point of 2000°C (2), and a boiling point of about 2800°C. Pure titanium is prepared industrially chiefly by the reduction of $TiCl_4$ with molten magnesium at about 850°C in steel reaction vessels, using helium or argon as a protective atmosphere (1-3). The majority of commercial titanium foils and sponges are contaminated, however, because of the great affinity of titanium for trace amounts of iron and aluminum.

Titanium is a grey metal, resembling steel in appearance (4,5). At low temperatures, it is fairly stable in air. Titanium metal is soluble in cold concentrated hydrochloric or sulfuric acid; more readily so when the acids are heated. It is not soluble in concentrated nitric acid, but is soluble in hydrofluoric acid. It is also soluble by fusion with potassium bisulfate, potassium pyrosulfate, sodium peroxide, and other alkalies (6). It can be ignited to TiO_2 at about 1200°C. Titanium is most readily attacked by the halogens. At higher temperatures, titanium also reacts readily with other nonmetals; some of the compounds thus formed are remarkable for their stability towards chemical reagents. Titanium is usually electropositive and quadrivalent in its compounds, but may also function as trivalent and in a few compounds as bivalent. Quadrivalent titanium is easily converted to pertitanate by H_2O_2 and zinc; iron and aluminum converts Ti^{+4} to the Ti^{+3} state.

2. Soluble Salts of Titanium

Titanium forms compounds in its valence states of +2, +3, and +4. The halides are all soluble in water with TiI_4 and $TiBr_3 \cdot 6H_2O$ (7) being very soluble. $TiCl_2$ and $TiBr_4$ decompose in water. $TiCl_4$ is a liquid (M.P., -30°C).

Titanium oxalate [$Ti(C_2O_4)_3 \cdot 10H_2O$] is another salt (8) soluble in water. Many of the titanium salts are soluble in mineral acids; concentrated sulfuric acid with heat is the best. Salts of titanium other than complexes hydrolyze readily in solution unless a fairly strong acidity is maintained.

3. Insoluble Salts and Coprecipitation Characteristics

Metatitanic acid [$TiO(OH)_2$ or H_2TiO_3] is a highly insoluble compound (9) forming a white precipitate when hot sodium hydroxide is added to a boiling solution of Ti^{+4}. When titanium alone is present, its precipitation is not complete since it is slightly soluble in an excess of the NaOH but in the presence of iron, all the titanium is coprecipitated. In the procedure a small amount of ferric chloride carrier should be added to the acid sample solution. This precipitate provides a useful separation from chromium, molybdenum, tungsten, vanadium, and phosphorus.

In the above precipitation sodium peroxide (powder) can be substituted for the sodium hydroxide. The advantage of sodium peroxide is to oxidize manganese and chromium to the highest valence state which forms soluble salts and thus separates easily from titanium.

Ammonium hydroxide may also be substituted for sodium hydroxide at ordinary temperatures. A precipitate of white, gelatinous titanic acid [$Ti(OH)_4$] forms, which is insoluble in an excess of the reagent, but readily soluble in dilute mineral acid. The same reaction when carried out at the boiling temperature gives rise to metatitanic acid that is difficultly soluble in acids.

The hydroxide precipitation can be recommended only as the preliminary radiochemical separation of Ti^{+4} for the analysis of manganese and chromium rich alloys.

Since there are few insoluble salts available for the determination of titanium, other elements are usually precipitated away from the titanium. For instance, the separation of titanium from the hydrogen sulfide group (6,10) is accomplished by precipitation of the latter by means of H_2S gas in dilute acid solution, preferably after the addition of tartaric acid. If the latter has been included, a further separation from iron, cobalt, nickel, and zinc can be effected by adding ammonium hydroxide to the filtrate and centrifuging.

Cupferron (11) precipitates titanium, vanadium, molybdenum, tungsten, thorium, and cerium with a yellowish brown color. The temperature must be kept low and the cupferron solution should be prepared just before use.

p-Hydroxyphenyl arsonic acid (12-14) has been found an advantageous reagent for separating titanium from many ions. Zirconium carrier can be used to coprecipitate tracer titanium although hydrogen peroxide must be absent during the procedure. The reaction should be carried out in boiling solution and a lengthy digestion of the white gelatinous precipitates is necessary to improve the decontamination.

Even in strongly acidic solution, ammonium phosphate (15) produces a white, difficultly filterable precipitate of more or less basic titanic phosphate of somewhat indefinite composition. Even in the presence of tartaric acid titanium can be precipitated as phosphate when the solution is boiled.

Potassium ferrocyanide gives a finely divided brown precipitate with this element while tannic acid produces a brown precipitate which soon turns orange-red in dilute acidic solution.

4. Complex Ions of Titanium

Titanium, mainly owing to its weak basicity (16), gives scarcely any normal salts of oxyacids, weak or strong. Thus, titanium forms no simple oxalate, nitrate, or sulfate.

Quadrivalent titanium has somewhat of a tendency to form anion complexes such as $[TiO_3]^=$, $[TiF_6]^=$, $[TiCl_6]^=$, and $[Ti(SO_4)_3]^=$ (17).

The stability of the complex halides falls off very rapidly with increasing atomic number of the halogen; only the fluorides have any considerable stability. These are, in general, not strongly complexed; they cannot be re-crystalized from pure water without undergoing hydrolytic decomposition.

5. Chelate Complexes of Titanium

Currently, there are not many organic reagents which are known to form chelate complexes with titanium. A few organic compounds of practical interest for separations of titanium are listed in Table I:

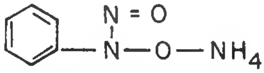
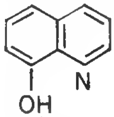
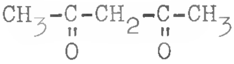
6. Extraction of Titanium

Ion association systems of solvent extraction are of little value for titanium separations because of the instability of the titanium complexes. However, advantage may be taken of this instability by separating out other interferring ions and leaving the titanium unaltered. For instance, Au, Ga, Fe, and Mo are easily taken out by ether extraction leaving Ti^{+4} untouched.

The other type of solvent extraction which is very useful in practice as a radiochemical separation is the chelation of the metallic cation in aqueous solution followed by solution of the organic chelate by the organic solvent. As mentioned in the previous section, the ammonium salt of N-nitrosophenylhydroxylamine (cupferron) is a good reagent to separate titanium in the chelate form from many other elements. Cu, Mo, W, and V are the only contaminants found spectrometrically.

The technique of the extraction is very simple and fast. When the organic solvent is contacted with 6% aqueous cupferron in a normal 150 ml separatory funnel, 92 to 95% of the Ti^{+4} extracts with one vigorous shaking. A 10% H_2SO_4 solution is recommended. Although there are other organic reagents such as oxine which are only selective at the certain pH, in this instance the acidity could be varied from 8-20%.

Table I. Separation of Titanium by Chelates

Chelate Agent	Conditions	Form	Reference
Cupferron 	10% HCl or H_2SO_4	Isopropyl ether or chloroform extract	a-h
8-Quinolinol (oxine) 	pH 3.5-5.0	Chloroform extract	h,i
Acetylacetone  $CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$	pH 0-1.6	Chloroform extract	j
7-Bromo-8-hydroxyquinoline-5-sulfonic acid	$>2N\ H_2SO_4$	ppt	k
5,7-Dibromo-8-hydroxyquinoline (Bromoxine)	pH 1.3-1.9	ppt	l

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Isopropyl ether or chloroform can be used as the solvent. Isopropyl ether works faster to give the separated organic and aqueous layer than chloroform. In addition, backwashing can be done with 15% NaOH to eliminate Cu, V, Mo, and W in the ether solution without more than a 15% loss of titanium. Furthermore, ether can be evaporated faster on a hot plate than chloroform thus producing higher counting samples for a given investment of time.

An excellent discussion on the uses of cupferron and particularly the behavior of many of the elements in the extraction is given by Furman, Mason, and Pekola (18). Welcher (19) gives a detailed picture of cupferron as an analytical reagent in his book.

White and Ross (20,21) report that 0.1 M, (4%), Tri-n-octylphosphine oxide (TOPO) in cyclohexane is selective extracting reagent for Ti^{+4} in 7 M H_2SO_4 solution. A 15-20 minute shaking or stirring time would, however, be required for extraction and the phases should be allowed to stand until they separate completely. (The rate of equilibrium is rather slow.) Under the above conditions the only interferences found were Cr(VI), Mo(VI), and Ce(IV) and these were quite a relatively low level.

Taylor (22) made an excellent study of the extraction of Ti^{+4} with 8-quinolinol (1% oxine in chloroform). Since 8-quinolinol (23) is only a selective reagent for titanium at pH of 3-5,the pH must be adjusted by adding 4% E.D.T.A. This E.D.T.A. (24) also serves as a good masking agent for the other elements. Tartaric acid must also be used to prevent the hydrolysis of titanium at a pH greater than 5. Charlot and Bezier (25) give a table of the pH range for precipitation of a number of elements for the reagent. McKavency and Freiser (26) have studied the extraction behavior of titanium with acetyl acetone in chloroform. The extraction is not selective and the percent recovery of titanium is low.

7. Ion Exchange Behavior of Titanium

Most of the separations carried out by ion exchange chromatography have been based on differences in the degree of dissolution of the substances being separated or on the stability of their complexes. Since titanium hydrolyzes readily even in acid solutions and has unstable complexes, it would seem to be necessary to use either very strong complexing agents, e.g., HF,or HCl-HF, or cation exchange based on the specificity of the resins for the elements to be separated. Because of these difficulties, relatively little is known about the ion exchange behavior of titanium.

Osborn (27) compiled a very good bibliography including all the papers up to June, 1953 in which he denoted two references for the ion exchange of titanium. One of them written by Brown and Rieman (28) showed that Ti^{+4} in concentrated HCl with 1% citric acid (pH~1.75) was separated from Zr and Th. A 7 cm bed with a cross section area of 7.07 cm^2 with a flow rate of 0.85 $ml/cm^2/min$ was used. A small amount of Dowex-50 was equilibrated with the solution and eluted. In applying the method to radiochemical separation of titanium, the flow rate is too slow and pH adjustment is tedious for a rapid separation; besides the selectivity of the elements is questionable. The other paper (29) dealt with the separation of titanium from iron. This is not a problem in radiochemical separation of titanium after activation because of the low activation cross-section of iron.

Chemical Abstracts, up to 1959 listed one paper (30) on the separation of Ti, W, Mo, and Nb by anion exchange.

In the study of titanium ion exchange, the oxides were fused with potassium bisulfate, and then dissolved in mixtures of various concentrations of hydrochloric and hydrofluoric acid. Kraus and Moore (31) have determined the elution constants for Zr, Hf, and Nb as a function of the concentration of HCl and HF. For titanium, quantitative separations could be effected by using the proper ratio of the acids.

Kallmann (32,33) has shown that when a cold hydrochloric acid solution of titanium is saturated with HCl gas (13 N) and then passed through an anion exchange resin, all of the titanium is absorbed while many contaminating ions pass through.

V. DISSOLUTION OF TITANIUM CONTAINING MATERIALS

The rapid and complete dissolution of titanium containing materials is required for radiochemical separation of titanium because of the short (5.8-minute) half-life.

A very effective procedure for attacking all kinds of samples (if powdered or burned to ashes) is a fusion with sodium peroxide (34) in a nickel crucible, followed by adding water, centrifuging and finally dissolution in acid. Sulfuric acid is recommended if a cupferron extraction is to follow. The procedure has two purposes. It gives not only rapid and complete decomposition of samples, but also separates titanium from chromium, molybdenum, tungsten, vanadium, manganese, and phosphorus.

For some silicate rocks, HF in conjunction with concentrated sulfuric acid works perfectly in 30 seconds.

Biological and botanical samples can be fused with potassium pyrosulfate. The fused material is then dissolved in sulfuric acid. A platinum crucible should be used. Concentrated nitric acid followed WITH CARE by 72% perchloric acid is also useful for effecting dissolution of organic samples in a shorter time.

Either sodium bifluoride or potassium bifluoride can also be used for certain samples.

Aluminum alloys are often easily dissolved in concentrated hydrochloric acid.

VI. COUNTING TECHNIQUES FOR THE TITANIUM NUCLIDES

There are only four radioisotopes of titanium known at present Among them, Ti^{43}, with a half-life of only 0.58 seconds, is too short to separate rediochemically; Ti^{44}, with longer half-life is little known. Ti^{45} can be produced by a (d,2n) reaction on a scandium target. Since it decays by both β^+ (~83%) and E.C. (~17%) it can be counted in either a scintillation well or Geiger-Müller counter. The β^+ decay can also be counted by a gas flow proportional counter or a NaI scintillation spectrometer since it gives off the 0.51 Mev annihilation radiation. This 3.1-hour isotope might be used as a tracer for titanium.

Ti^{51} is easily produced by the (n,γ) reaction and it decays with two β^- rays (2.1 Mev, 94.5%; 1.5 Mev, 4.5%) and three gamma rays (0.32, 0.93, and 0.61 Mev). The 0.32 Mev γ-ray is very distinctive while the other two are hardly noticeable unless a large amount of titanium is counted. A gamma spectrometer with a 1-3/4" x 2" thallium activated NaI crystal is well fitted to count the 0.32 Mev γ-ray of Ti^{51}. The advantage of the smaller crystal over the 3" x 3" crystal is to give higher resolution and the better efficiency for the lower energy gamma.

However, a 3" x 3" crystal can be used not only for detecting the low energy γ-ray, but also for checking more efficiently the contamination from higher energy gamma rays. A γ-ray spectrum of Ti^{51} taken under these conditions is given in Figure 1. Either a liquid or solid sample can be used for this purpose without worrying about self-absorption. In a standard 1-3/4" x 2" scintillation well counter, when about 10 ml of sample in a 3/4" x 6" test tube is counted, the counting efficiency is about 20-22%.

The β^-rays of Ti^{51} can be counted by a standard Geiger or proportional counter. The high energy (2.1 Mev) minimizes problems of self-absorption in samples of a few milligrams.

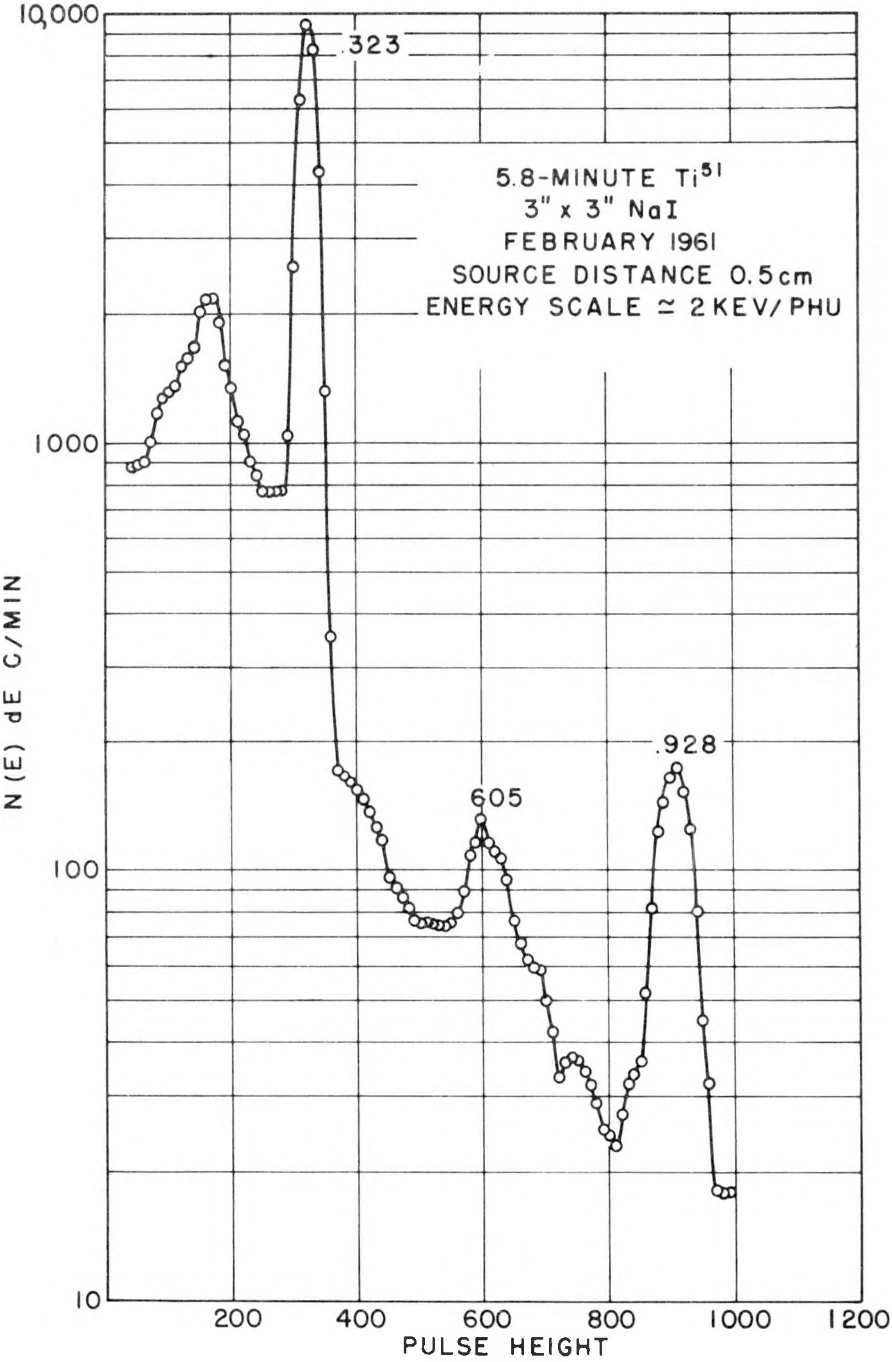

Figure 1. Gamma ray spectrum of Ti^{51}.

VII. COLLECTED RADIOCHEMICAL SEPARATION PROCEDURES FOR TITANIUM

The importance of radiochemical separations for many of the elements rests in use in fission product analysis. In contrast, the radiochemical separation of titanium is used mainly for detecting and determining trace amounts of titanium in various samples and in separations of tracer titanium from cyclotron bombardments.

For this use the determination must give higher sensitivities than the colorimetric determination and must be simple and fast so as to be able to compete with other determinations. Since Ti^{51} has a 5.8-minute half-life, it is desirable to complete the separation in 6 to 12 minutes (one or two half-lives) to obtain best sensitivity.

Actually very little work has been done on the radiochemistry of titanium and it is hoped the few procedures developed here for activation analysis and outlined below can serve as a catalyst for development of further procedures for bombardment chemistry.

PROCEDURE 1

Source - C. K. Kim, University of Michigan

Element separated: Titanium

Target material: Meteorites, rocks and minerals, alloys, botanical and biological ashes.

Type of bbdt: Neutron activation; 15 minute irradiation at 10^{12} n cm^{-2} sec^{-1}

Time for sep'n: 13 minutes

Equipment required: 30 ml nickel crucible with a lid, Fisher burner, centrifuge, separatory funnel.

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 1); fuse 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 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 precipitate 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:

(1) 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 attached by the peroxide.

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

(3) The temperature should be kept low (~ $10^\circ C$) preceeding 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 a limited separation time may result in incomplete fusion.

(4) 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.

(5) 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 (~ $10^\circ C$) so as not to destroy the cupferron. Often, the heat involved in the neutralization with NaOH will cause trouble.

(6) 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 shouldbe used instead of the normal 420 mμ for photometric determination.

(7) 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.

(8) 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%.

PROCEDURE 2

Source - C. K. Kim, University of Michigan

Element separated: Titanium

Time for sep'n: ~ 10 min.

Target material: Meteorites, rocks and minerals; biological and botanical samples

Equipment required: Standard plus 30 ml nickel crucible and sintered glass filter with chimney.

Type of bbdt: Neutron activation

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-hydroxy-(phenyl)-arsonic 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)(35).

Notes:

(1) For a sample abundant in chromium, an anion exchange column should be used to adsorb Cr^{+6} ions.

PROCEDURE 3

Source - C. K. Kim, University of Michigan

Element separated: Titanium

Target material: Aluminum alloy

Type of bbdt: Neutron activation

Yield: >5 - 85%

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

Advantages: Rapid separation

Time for Sep'n: ~11 min.

Equipment required: Standard

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)(35).

Notes:

(1) 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

Element separated: Titanium	Time for sep'n: 12 minutes
Target material: Botanical and biological samples.	Equipment required: Standard

Type of bbdt: Neutron activation

Yield: 90%

Degree of purification: Fairly good for γ-spectrometry

Advantages: Fast and simple

PROCEDURE 4 (Continued)

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 precipitate $Fe(OH)_3$ 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)(35).

Notes:

(1) 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, 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 expells 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.

(2) 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

Element separated: Titanium	Time for sep'n: 17-20 minutes
Target material: NBS Ferrochromium alloy containing 0.034% Ti.	Equipment required: Standard 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.

(4) Add Zr carrier and precipitate with p-hydroxy-phenyl-arsonic 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-octyl phosphine 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:

(1) 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 (21).

(2) 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.

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