TITANOUS SOLUTIONS FROM METALLIC TITANIUM

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TITANOUS SOLUTIONS FROM METALLIC TITANIUM

By

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DEDICATION

To Doctor Elmer Leininger, whose kind help and efficient direction was so unstintingly given, this thesis is gratefully dedicated.

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INTRODUCTION

INTRODUCTION

The advent of titanium on the industrial scene as a structural metal has become of increasing importance in recent years. Its use is even more striking when its cost is considered. At the present moment E. I. du Pont de Nemours and Company supplies titanium metal having a purity of greater than 99.5 percent. Sponge metal costs $7.50 per pound in pound lots, while ingot metal is $15.00 per pound in pound lots (2).

The combination of qualities which are possessed by titanium are several. Its weight is intermediate between aluminum and iron, but nevertheless it has an excellent strength-to-weight ratio (2). Thus for structural applications in which lightness combined with strength is an important factor, the use of titanium or titanium alloys shows a very promising future.

Perhaps the most outstanding physical property of titanium is its resistance to corrosive substances. Tests have shown that commercially pure titanium is resistant to boiling glacial acetic acid, boiling 10 percent sodium hydroxide, warm concentrated nitric acid, and relatively dilute warm hydrochloric and sulfuric acids. There are also indications that a passive film is formed on titanium by boiling nitric acid which is very resistant to further attack by the acid. Salt spray tests, conducted over a period of 1000 hours, have exhibited no visible effect (2).

In its reactions with gases, titanium is quite active. It readily forms adherent and relatively impermeable oxide and nitride coatings at

temperatures up to 1300° F. At higher temperatures the metal dissolves in its own oxide, and will in time become embrittled. Hydrogen, however, behaves quite differently than does oxygen and nitrogen. At temperatures above 600° F, hydrogen is absorbed interstitially by titanium. The absorbed gas may be removed by heating the metal in a high vacuum at elevated temperatures (2).

Most of the present-day titanium produced in the United States is made by the Kroll process. The method consists of reducing the purest grade of titanium tetrachloride available to metallic titanium by magnesium. Following the reduction, the resultant spongy mass of metal is leached with dilute hydrochloric acid to remove unreacted magnesium and magnesium chloride.

The actual reduction is accomplished in a molybdenum-lined iron vessel, under an atmosphere of argon. The inert gas is necessary to protect the metal, particularly when hot, from oxygen and nitrogen. It has been shown that the properties of ductile titanium are affected adversely by a factor of up to 20 by these gases dissolved in the metal as compared to the same amount of metallic impurities in the metal (12).

With the availability of a consistently good quality of titanium metal assured, it was thought that a study of titanous solutions derived from the metal would be of interest.

It had been noted that in the preparation of titanous sulfate solutions used to regenerate Walden silver reductors in the student laboratories, the solutions seemed to be largely composed of titanium (III). It was decided to determine to what extent the titanium was present in

the trivalent state. If it were present quantitatively as titanium (III), this fact could be used to prepare standard titanous reducing solutions.

References in the literature to the spectrophotometric characteristics of titanous solutions are very scanty.

Therefore, the purpose of this thesis is twofold: 1) to study the preparation of titanous solutions directly from titanium metal and 2) to investigate the spectrophotometric properties of titanous solutions.

HISTORICAL

HISTORICAL

In the hydrogen sulfide scheme of qualitative analysis, titanium is found in the "ammonium sulfide" group, provided that a sufficient quantity of strong acid is present to prevent its prior hydrolysis and consequent precipitation.

The oldest methods of determining titanium were gravimetric, and based upon the ease with which tetravalent titanium salts were hydrolyzed and precipitated. The hydrous oxide is quantitatively precipitated at a pH of 2.0 (13). The adjustment of the pH of the solution may conveniently be made with ammonium hydroxide, sodium hydroxide, sodium carbonate, or any other alkaline compound.

Titanic ions are precipitated by phosphate in acid solution, at a pH of about 2. However, this method of determination has some undesirable features. The precipitate of titanic phosphate is very gelatinous and difficult to filter and wash. In addition the composition of the ignited precipitate varies according to the acid in the solution from which the precipitation is made (5).

Cupferron precipitates titanium as a rather voluminous, flocculent, golden precipitate, even in strong mineral acid solutions (6). Ferric iron is also precipitated under these conditions.

According to Pribil and Schneider (8), tetravalent titanium may be precipitated by ammonium hydroxide from solutions containing aluminum and ferric iron by complexing the latter with the di-sodium salt of ethylene diamine tetraacetic acid (Versene). The precipitate of the hydrous oxide of titanium is ignited to titanium dioxide.

Volumetric methods for the determination of titanium are dependent upon the redox reactions of the element.

A direct method, requiring no preliminary reduction, is the titration of titanium (IV) with standard chromium (II), using a potentiometrically determined endpoint (4).

The complete conversion of tetravalent titanium to its trivalent state requires a powerful reductant. Bischoff (1) accomplished this by reducing titanium salts with pure electrolytic iron in a carbon dioxide atmosphere. He claimed that twenty equivalents of iron were necessary for the quantitative reduction, and that the presence of ferrous iron appeared to stabilize the solution against air oxidation. After all the iron had dissolved, the titanous solution was titrated with standard ferric chloride, using potassium thiocyanate as an indicator.

Emi and Doi (3) state that titanium (III) is more resistant to air oxidation in sulfuric acid solution than in hydrochloric acid solution.

Syrokomskii and Silaeva (9) assert that acetic acid and ammonium sulfate form complexes with titanium (III) in aqueous solution which render it less sensitive to air oxidation. After reducing titanium in a bismuth reductor, they complete the procedure by titrating with standard ceric sulfate, using cacotheline as an indicator. They claim that it is not necessary to protect the solution with an inert atmosphere during the titration.

Jonnard (7) in a review article, refers to several methods of preparing titanous solutions. The use of metallic calcium, zinc in sulfuric acid solutions, sodium amide, hydrogenation using a platinum catalyst, and electrolytic reduction are discussed.

A method of analyzing commercial titanium metal has been reported by Thompson (10). The sample is dissolved in potassium acid sulfate and a little sulfuric acid. After complete dissolution, the cooled melt is dissolved in dilute hydrochloric acid solution. A preliminary reduction is accomplished by use of zinc amalgam, after which it is passed through a Jones reductor. The titanous solution is titrated under an inert atmosphere with standard ferric chloride.

The determination of small amounts of titanium is best accomplished by colorimetric means. In sulfuric acid solution, titanium (IV) gives an intense yellow color upon the addition of hydrogen peroxide (11).

EXPERIMENTAL

Reagents Used

1. Titanium metal (sponge) -- Supplied by E. I. du Pont de Nemours and Company, Incorporated.
2. Potassium dichromate -- Mallinckrodt Primary Standard grade, checked against a sample supplied by the National Bureau of Standards (Number 136).
3. Ferric chloride -- Baker and Adamson reagent grade. A 0.1 normal solution, made by dissolving 27.0 g. of the hexahydrate in a liter of solution containing 10 ml. of hydrochloric acid, was standardized according to the method of Willard and Furman (14).
4. Ceric ammonium sulfate -- Supplied by the G. Frederick Smith Chemical Company, Columbus, Ohio. A 0.1 normal solution is made by dissolving 63 g. of the dihydrate in a liter of one normal sulfuric acid. The solution is standardized against arsenious oxide (15).
5. Arsenious oxide -- Baker and Adamson Primary standard grade, lot number G020.
6. Citric acid -- Merck reagent grade.
7. Sodium diphenylamine sulfonate -- A 0.01 molar solution of the indicator was prepared (16).
8. Ferroin indicator -- A 0.025 molar solution, supplied by the G. Frederick Smith Chemical Company was used.
9. Amalgamated zinc -- Supplied by the G. Frederick Smith Chemical Company.

Preparation and Analysis of Titanous Solutions

One of the advantages of titanium, namely its superior resistance to acids and other corrosion-causing agents, is an inherent difficulty when the problem of dissolving the metal preparatory to an analysis is considered. Since the element is practically impervious to the action at room temperature of any single mineral acid except hydrofluoric, it was first necessary to conduct some preliminary qualitative tests to find a satisfactory medium in which to dissolve the sample.

To this end the following solvents were used:

1. Sulfuric acid (1 part of acid to 1 part of water). The metal dissolved readily at first, but soon part of the water evaporated. At this point titanous sulfate crystallised from the solution, and coated the undissolved metal to such an extent that the solvent action of the acid soon stopped.

2. Sulfuric acid (1:4). The action of this solvent was appreciably slower, but nonetheless effective. The difficulty of salts crystallising from the solution was not encountered in this case.

3. Hydrochloric acid (1:1). The dissolving action of this acid was somewhat slower than that of the 1:1 sulfuric acid.

4. One part water -- 1 part sulfuric acid -- 1 part hydrochloric acid -- 0.5 parts of phosphoric acid. This solvent had the quickest dissolving action upon the titanium. As the sample approached the stage of being completely in solution, it had disintegrated into many particles, which were so small as to be barely visible were it not for the bubbles of hydrogen evolved from their surfaces.

5. Ten g. potassium sulfate acid -- 5 ml. concentrated sulfuric acid. In the solvent the titanium sample initially dissolved quite readily, but soon the action decreased considerably, and finally ceased altogether. This was due to the formation of titanous sulfate on the surface of the exposed metal, which very effectively protected it from the action of the solvent. The fused mass was light yellow while hot; upon cooling it turned white. When dissolved in water, no blue color was imparted to the solution, indicating the absence of any trivalent titanium.

It had been noted in these preliminary tests that the solutions resulting from the dissolving of titanium in non-oxidising acids were the typical blue color of trivalent titanium. Accordingly, it was decided to ascertain whether this fact would furnish a means of determining the percentage purity of the sample.

To insure complete protection from air oxidation, the apparatus in Figure I was used.

A is a 500 ml. wash bottle, into which was placed a solution of titanous sulfate, and so arranged that the inert gas bubbled through the solution before making its exit. B is a 250 ml. glass stoppered (standard taper) iodine flask, containing the sample and the solvent. C is a four inch adapter tube, with one end standard taper to fit into the iodine flask. D, a 60 ml. separatory funnel, was connected to the adaptor tube with a two-hole rubber stopper. The remaining hole was fitted with a piece of right angle glass tubing, the outside end of which was connected to the rubber tubing coming from the titanous sulfate

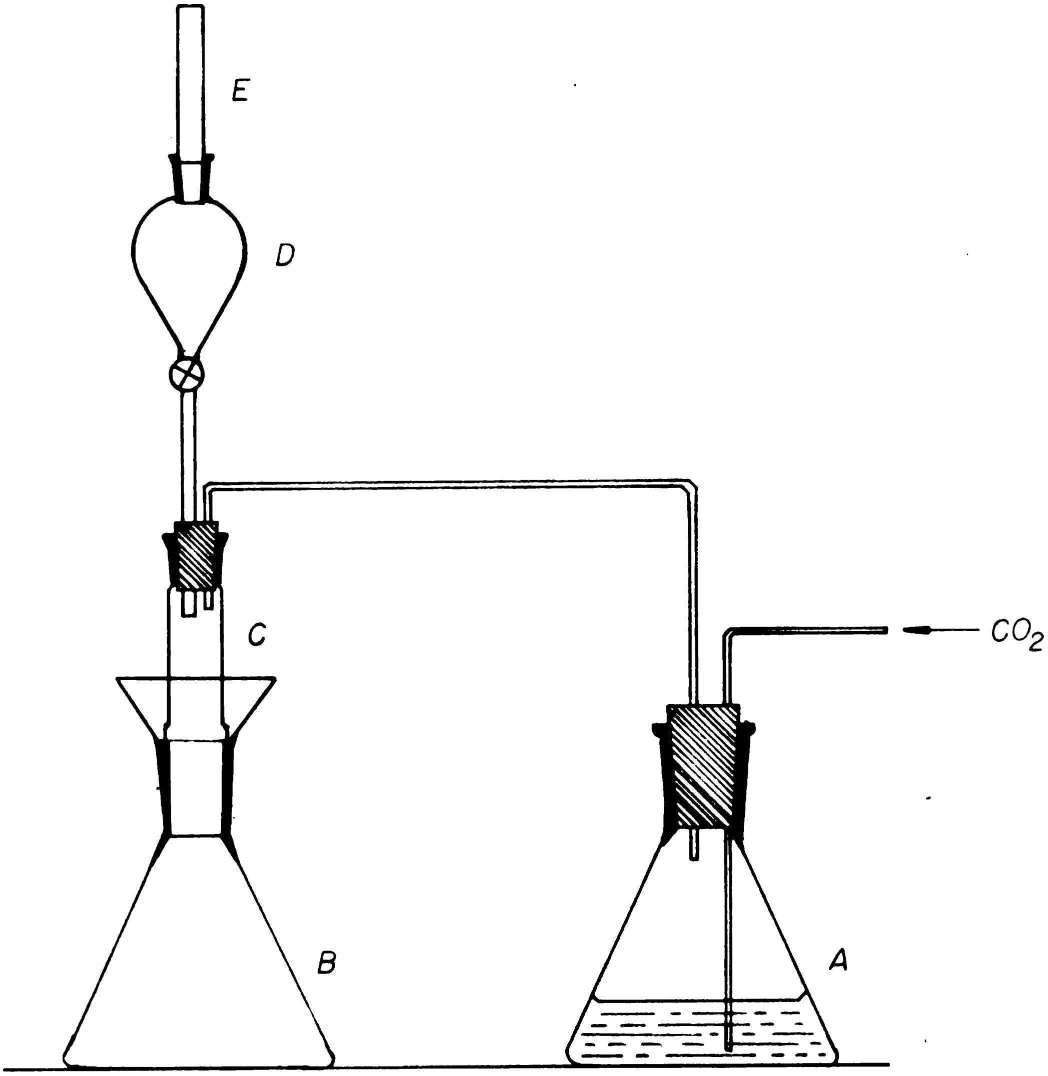


FIGURE 1

DISSOLVING APPARATUS

wash bottle. The only piece of rubber in the apparatus is a considerable distance away from the solution, and it is therefore very unlikely that any of the titanous solution would come into contact with it. Into the ground glass top of the separatory funnel was inserted E, a six inch male ground joint. This last piece of apparatus was necessary to prevent liquid condensing in the separatory funnel from being spattered around the area. This spattering is caused by the inert gas bubbling up through the system.

Two separate inert gases were used, nitrogen and carbon dioxide. These were supplied from steel cylinders. In order to insure the removal of any traces of oxygen present in the gases, they were passed through the preliminary scrubbing flask.

A sample of about 0.2 g. of titanium was accurately weighed and placed in the iodine flask. Thirty ml. of the solvent (10 ml. water, 10 ml. sulfuric acid, 10 ml. of hydrochloric acid, and 5 ml. of phosphoric acid) was introduced through the dropping funnel, and the inert gas allowed to pass into the flask and escape through the funnel. The contents of the flask were heated to quiet boiling on a hot plate. The complete dissolving of the sample took from about an hour to an hour and a half. Since the weight of sample was composed of from four to six small pieces of metal, the resistance of titanium to acids of even this concentrated strength is easily apparent.

Following complete solution of the sample 50 ml. of a roughly 0.1 normal solution of ferric chloride was placed in the dropping funnel, and the apparatus removed from the hot plate. The flow of inert gas was stopped, and most of the ferric chloride was drawn into the flask by the reduction of pressure caused by the cooling of the flask and its contents. However, it was usually necessary to remove the rubber tubing in order to allow the complete introduction of the ferric chloride solution. The ferric chloride was washed into the flask with a few milliliters of water, thereby leaving the upper part of the apparatus clean and in readiness for use with another sample.

As the ferric chloride oxidized the titanous ion present to titanic ion, a heavy white gelatinous precipitate of titanic phosphate slowly formed, over a period of perhaps a minute.

The resulting ferrous ion produced by the oxidation of the titanous ion was titrated with 0.1000 normal potassium dichromate, using the sodium salt of diphenylamine sulfonic acid as the indicator. The color change, from green to dark blue, was readily discernable, in spite of the copious precipitate of titanic phosphate present in the solution. An indicator correction of 0.05 ml. was applied in each case.

The results in Table I were calculated as percent purity of the titanium, as follows:

$$\text{Percent titanium} = \text{ml. reagent} \times \text{normality} \times 0.04790 \times \frac{100}{\text{wt. sample}}$$

To avoid the precipitate of titanic phosphate subsequent to the addition of ferric chloride, the effect of citric acid, a well-known complexing agent, was studied. Insofar as preventing tetravalent titanium from precipitating in the acid solution, the citric acid was successful. An amount of about 200 mg. of citric acid was used.

TABLE I

DETERMINATION OF PURITY OF TITANIUM BY TITRATING WITH STANDARD POTASSIUM DICHROMATE

Sample	Weight (g)	$K_2Cr_2O_7$ (ml)	Titanium %
1	0.2072	43.16	99.76
2	0.2016	41.95	99.67
3	0.2222	46.24	99.23
4	0.1807	37.57	99.5

However, the citric acid failed on two other counts. The indicator endpoint was not nearly as sharply defined as with phosphoric acid, and a far more serious factor was the fact that the citric acid slowly reduced the dichromate. Consequently, any titration with the standard reagent was meaningless. This relatively slow oxidation of citric acid by dichromate is illustrated in Table II.

TABLE II

OXIDATION OF CITRIC ACID BY POTASSIUM DICHROMATE

Sample	$FeSO_4$ (ml)	$K_2Cr_2O_7$ (ml)	$K_2Cr_2O_7$ Reduced (ml)	Time (min)
1	5.00	0.42	1.99	0
2	5.00	0.53	2.01	5
3	5.00	1.37	2.34	10

Each sample was identical, and consisted of 5.00 ml. of potassium dichromate, 200 mg. of citric acid, 25 ml. of water, and 5 ml. of sulfuric acid. After standing for the indicated period of time, 5.00 ml. of ferrous sulfate was added, 6 drops of sodium diphenylamine sulfonate indicator, and the solution titrated to the customary endpoint. Since the ferrous sulfate had been standardized and found to be exactly equivalent to the potassium dichromate, the amount of dichromate reduced by the citric acid may be found by subtracting the 5.00 of ferrous sulfate pipetted into the solution from the total number of milliliters of dichromate used. It is thus apparent that citric acid is slowly oxidized by dichromate under the conditions necessary to titrate ferrous ion with dichromate.

In order to dispense with the use of phosphoric acid, necessary in the titration of ferrous ion with dichromate, the procedure was modified to some degree, in that cerate was used as the titrating agent, with ferroin as the indicator. The composition of the acid solvent was changed, with water being substituted for phosphoric acid.

However, the process of dissolving the metal under an inert atmosphere was not altered, nor was the oxidation of trivalent titanium to tetravalent titanium using ferric chloride changed.

Because of the sharpness of the endpoint and its sudden appearance with little warning, a small quantity of the reduced solution was withdrawn in a small medicine dropper at the beginning of the titration. After the color change from red to colorless had taken place, this amount was washed back into the main body of solution, and the final endpoint cautiously obtained dropwise. Throughout the course of this work, several lots of cerate solution were prepared and standardized, accounting for the different normalities in the following table. The results of the cerate titrations are itemized in Table III. As before, the results are calculated as the percent purity of the metal.

TABLE III

DETERMINATION OF PURITY OF TITANIUM BY TITRATING WITH STANDARD CERATE

Sample	Weight (g)	N Cerate	Cerate (ml)	Titanium %
1	0.1824	0.0943	40.22	99.60
2	0.1644	0.0943	36.35	99.87
3	0.2062	0.0943	45.60	99.89
4	0.1827	0.0943	40.29	99.61
5	0.1689	0.1083	32.49	99.75
6	0.2112	0.1083	40.45	99.31

Several titrations using cerate were made using the original acid solvent containing phosphoric acid. There was no significant difference in these results when compared with solutions containing no phosphoric acid. However, another difficulty, in addition to the precipitation of titanic phosphate, was the precipitation of ceric phosphate. Therefore, after each addition of reagent, sufficient time had to be allowed for the precipitate of ceric phosphate to react. In spite of these precautions, satisfactory results were obtained, as indicated in Table IV.

Because of the length of time necessary to dissolve the sample, it was decided to see if this length of time could be shortened by the use of a catalyst. Many transition elements, and particularly those of the platinum group, exhibit the property of increasing the speed of these types of reactions in which the evolution of hydrogen is involved.

TABLE IV

TITRATIONS OF TITANOUS SOLUTIONS CONTAINING PHOSPHORIC ACID

Sample	Weight (g)	N Cerate	Cerate (ml)	Titanium %
1	0.2155	0.1083	41.33	99.45
2	0.1531	0.1083	29.46	99.78
3	0.1736	0.1083	33.30	99.47

A stock solution of chloroplatinic acid was made up having a concentration of 0.01 mg. of platinum per milliliter. Various small amounts of this solution were added to the acid solvent and the time required to dissolve the sample noted. In general, the time was cut down by about a quarter. However, as may be seen from Table V, the results of the determinations were very erratic. It is presumed that the presence of the platinum makes the titanous solution much more sensitive to air oxidation, since the actual amount of the catalyst added is not sufficient in itself to oxidize the titanous ion, which is of course present in overwhelming abundance as compared to the platinum.

TABLE V

EFFECT OF PLATINUM CATALYST ON ACCURACY OF THE DETERMINATION OF TITANIUM

Sample	Weight (g)	Drops of Platinum	Cerate (ml)	Titanium %
1	0.1829	3	40.16	99.18
2	0.1878	4	41.13	99.65
3	0.2084	5	39.51	98.31
4	0.2115	3	40.32	98.85
5	0.2034	2	39.81	99.20

To test the validity of the values obtained for the percent purity of the titanium, the metal was determined using a standard method. In this case the sample was dissolved in 1:4 sulfuric acid and passed through a Jones reductor. The reduced solution was caught immediately in an excess of ferric chloride and the equivalent amount of ferrous ion was titrated both with standard potassium dichromate, and with standard cerate. In each case the appropriate indicator was used. The results are tabulated in Table VI.

TABLE VI

DETERMINATION OF TITANIUM USING THE JONES REDUCTOR

Sample	Weight (g)	N $K_2Cr_2O_7$	N Cerate	Reagent (ml)	Titanium %
1	0.1839	0.1000		38.33	99.84
2	0.1842	0.1000		38.22	99.39
3	0.2070		0.0908	47.39	99.59
4	0.1994		0.0908	45.76	99.82
5	0.1904		0.1083	36.60	99.68

In connection with these and other results it might be well to indicate the difficulty of obtaining a representative sample of titanium. The metal used in this work varied in size from small dust-like particles to large lumps weighing several grams. The metal is spongy and quite ductile, so that it was impossible to grind up a large amount and from that choose a representative sample. Consequently pieces of titanium approximating the size of a small pea were used to make the titanous solutions. Because of this arbitrary method of choosing the sample, it cannot be positively stated that a given solution represents a homogeneous portion of the entire available batch of titanium.

For example, the results of five determinations using the Jones reductor average out to be 99.62 percent, while those determinations, thirteen in all, made by dissolving the titanium directly in an inert atmosphere, have an over-all average of 99.61 percent. It may therefore be seen that while there is disparity among individual samples, the average purity of the batch of metal used is quite consistent.

The promise shown by these results seemed to indicate that an analyzed sample of titanium metal could be dissolved, using the proper precautions, and be employed as a standard solution.

To this end, therefore, a ferric chloride solution was standardized by reduction with stannous chloride, removal of the slight excess of stannous ion with mercuric chloride, and oxidation of the ferrous ion with standard potassium dichromate. The average of three determinations gave the normality of the ferric chloride solution as 0.1008.

For the dissolving of the titanium sample, a 250 ml. Pyrex volumetric flask was substituted for the iodine flask, coincident with the omission of the adaptor tube. Thus the sample could be dissolved, and after cooling, diluted to volume, with no exposure at any time to the oxygen of the air.

The water used for dilution purposes was treated so that it contained no dissolved oxygen. First it was boiled, after which sodium carbonate was dissolved in it. Then just before being used for diluting, it was acidified with concentrated hydrochloric acid, and briskly stirred, so that the escaping carbon dioxide gas saturated the solution. It was necessary to acidify the water in order to prevent the precipitation of hydrous titanous oxide when diluting the dissolved sample to volume.

All the time the dissolved sample was cooling, a stream of carbon dioxide was allowed to pass over its surface. Once at room temperature, the solution was brought almost to the mark by introducing the dilution water directly through the separatory funnel. The final adjustment was made with a medicine dropper after removal of the funnel. The final solution was mixed thoroughly.

After mixing, the buret was filled with the titanous solution, and titrations of the standard ferric chloride were conducted. The indicator used for these determinations was ten ml. of a 400 g. per liter solution of sodium thiocyanate, with the color change going from red to colorless. The indicator was not added to the titrated solution until a point about two or three milliliters from the endpoint. Results are shown in Table VII. In each case the normality of the titanous solution is calculated on a basis of the metal being 99.6 percent pure.

In view of the results obtained by directly dissolving titanium, it is difficult to explain the fact that the error involved in the determinations in Table VII are always negative. At first it was thought that dissolving the sample in a Pyrex volumetric flask might possibly be not as satisfactory as dissolving it in an iodine flask.

However, the titanium content of two samples was determined by dissolving in a Pyrex flask, oxidizing with ferric chloride, and subsequent titrating of the equivalent amount of ferrous produced with standard

TABLE VII

USE OF TITANOUS CHLORIDE AS A STANDARD SOLUTION

Sample	Weight (g)	$FeCl_3$ (ml)	$TiCl_3$ (ml)	N $TiCl_3$ Calculated	N $TiCl_3$ Found	Error, Parts per Thousand
1	0.6380	19.97	38.21	0.0531	0.0527	-8
2	0.6227	19.97	39.16	0.0518	0.0514	-8
3	0.6584	19.97	36.91	0.0548	0.0545	-6
4	0.6186	19.97	39.39	0.0515	0.0511	-8
5	0.6113	19.97	39.81	0.0509	0.0506	-6

cerate solution. The two values found were 99.85 and 99.60 percent, indicating that the dissolving process was not at fault.

Another possibility is that the titanous solution is oxidized while being transferred from flask to buret. This would have to be done in a fairly reproducible way to account for the consistency of the negative error.

Studies to show the relative stability of titanous solutions were also conducted. A solution of titanous chloride was allowed to stand for a period of time in a volumetric flask, with no attempt made to protect it from air oxidation. After sufficient solution had been withdrawn to fill the buret, the stopper of the flask was replaced, but no carbon dioxide was circulated through the flask to displace the air drawn into the flask in the transferring process. In this way the actual conditions during a series of titrations would prevail. The titanous solution was allowed to stand for twenty-four hours under a carbon dioxide atmosphere before the first samples were withdrawn. As indicated in

Table VIII, the solution is quite stable for a reasonable length of time. In each case, 19.97 ml. of titanous chloride was titrated with standard ferric chloride, using thiocyanate as indicator. The weight of sample was 0.6349 g. having a calculated normality of 0.0529.

TABLE VIII

STABILITY OF A TITANOUS CHLORIDE SOLUTION

Time (hrs)	$TiCl_3$ (ml)	$FeCl_3$ (ml)	N $TiCl_3$
24	19.97	10.37	0.0523
34.5	19.97	10.29	0.0519
47	19.97	10.05	0.0507
57	19.97	9.82	0.0496
72	19.97	9.40	0.0475

It may be observed that as titanous solution is withdrawn from the flask, the surface area of the solution exposed becomes greater, leading to a more rapid oxidation of the solution. In addition, the absolute amount of oxygen in the flask increases, also accelerating the rate of oxidation.

A similar study of a titanous sulfate solution was made. The results were very erratic, and varied from titration to titration, even when they were run one after another. Four titrations, successively made within five minutes of the previous one, dropped in normality from 0.0510 for the first, to 0.0495 to the last, as shown in Table IX.

TABLE IX

STABILITY OF A TITANOUS SULFATE SOLUTION

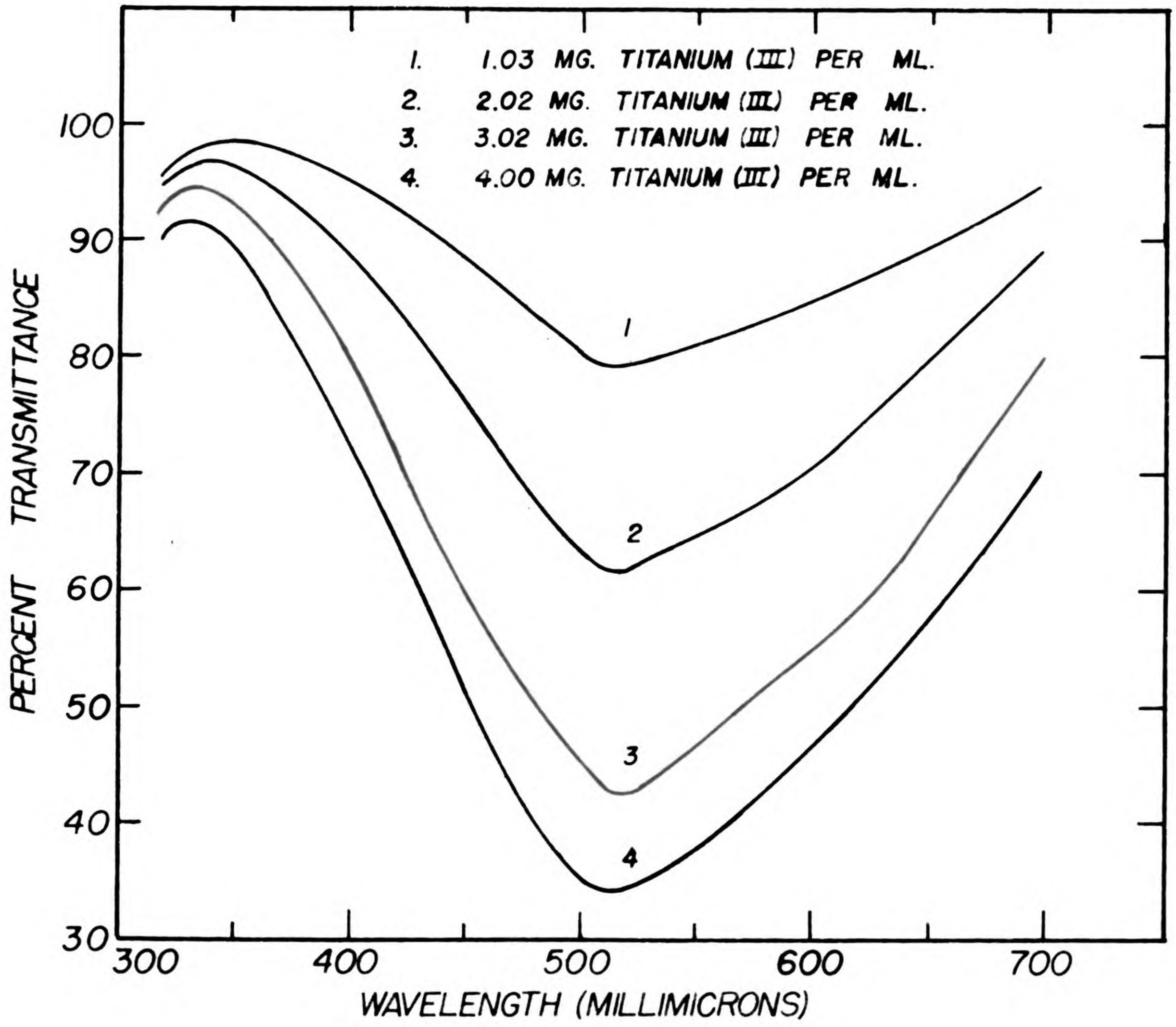
$Ti_2(SO_4)_3$ (ml)	$FeCl_3$ (ml)	N $Ti_2(SO_4)_3$
39.49	19.97	0.0510
39.74	19.97	0.0507
40.03	19.97	0.0503
40.64	19.97	0.0495

Spectrophotometric Studies of Titanous Solutions

Because of the blue color of titanous solutions, it was natural to make a spectrophotometric study of their properties.

The instrument used was a Beckman quartz spectrophotometer, Model DU. Corex cells having a light path of 1.000 cm. were employed to contain the various solutions. Measurements were made over a spectral range of 320 to 700 millimicrons. Water was used as a solvent blank. Graph I shows a family of curves for solutions containing varying amounts of titanous sulfate dissolved in one molar sulfuric acid. It may be observed that the curves are regular and smooth, with the minimum transmission at 520 millimicrons. An increase in the concentration of titanium causes no shift of the point of minimum transmittancy.

While making these determinations, a curious fact was noted. Upon standing for a period of time, the transmittancy of titanous solutions decreased. At first this was thought to be due to formation of a collodial dispersion of titanic oxide, caused by air-oxidation of the titanous



GRAPH I. SPECTRAL TRANSMITTANCE CURVES FOR TITANIUM (III) IN M H_2SO_4

solutions. To discover the truth of this matter, a stream of oxygen was allowed to bubble through a sample of titanous sulfate until the blue color had disappeared. The transmittancy of this solution was measured, and found to be 100.1 percent. It was therefore concluded that no collodial dispersion of titanium (IV) oxide was formed.

The cause of this apparent discrepancy is at present unknown. However, it is possible that titanous and titanic sulfate form a more deeply colored complex than either of the two salts alone. Eventually all the titanous sulfate is air-oxidised, the complex is destroyed, and since titanic sulfate is colorless, the transmittancy of the solution attains 100 percent.

Thus there are two opposing factors at work. The complex tends to make the solution transmit less light, while the titanic sulfate formed by air oxidation is colorless. Therefore, over a period of time, the transmittancy of a solution of titanous sulfate would decrease to a minimum value, after which it would increase until all the titanous sulfate was oxidised.

The data in Table X represent a sample of titanium whose transmittancy and titanous content was measured over a period of time. The transmittancy was measured at 520 millimicrons; immediately after the observation the titanous content of the solution was determined by titration with standard cerate. As indicated in the table, the transmittancy and titanous content both decrease.

It thus is apparent that if any quantitative meaning is to be derived from spectrophotometric measurements of titanous solutions, they

TABLE X

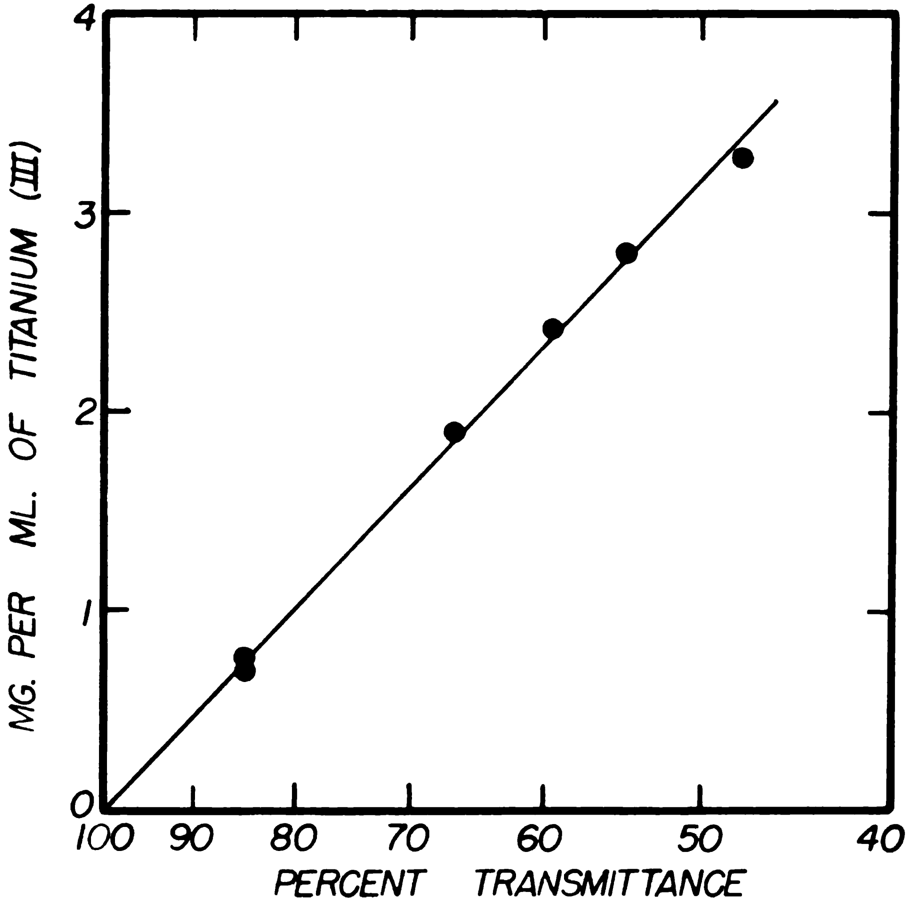
COMPARISON OF TRANSMITTANCY AND TITANOUS CONTENT OF A TITANOUS SULFATE SOLUTION

Time (hrs)	Transmittancy	Mg. Ti per Ml.
0	54.5	2.80
16	50.0	2.78
65.5	39.8	2.61
92.5	31.0	2.45

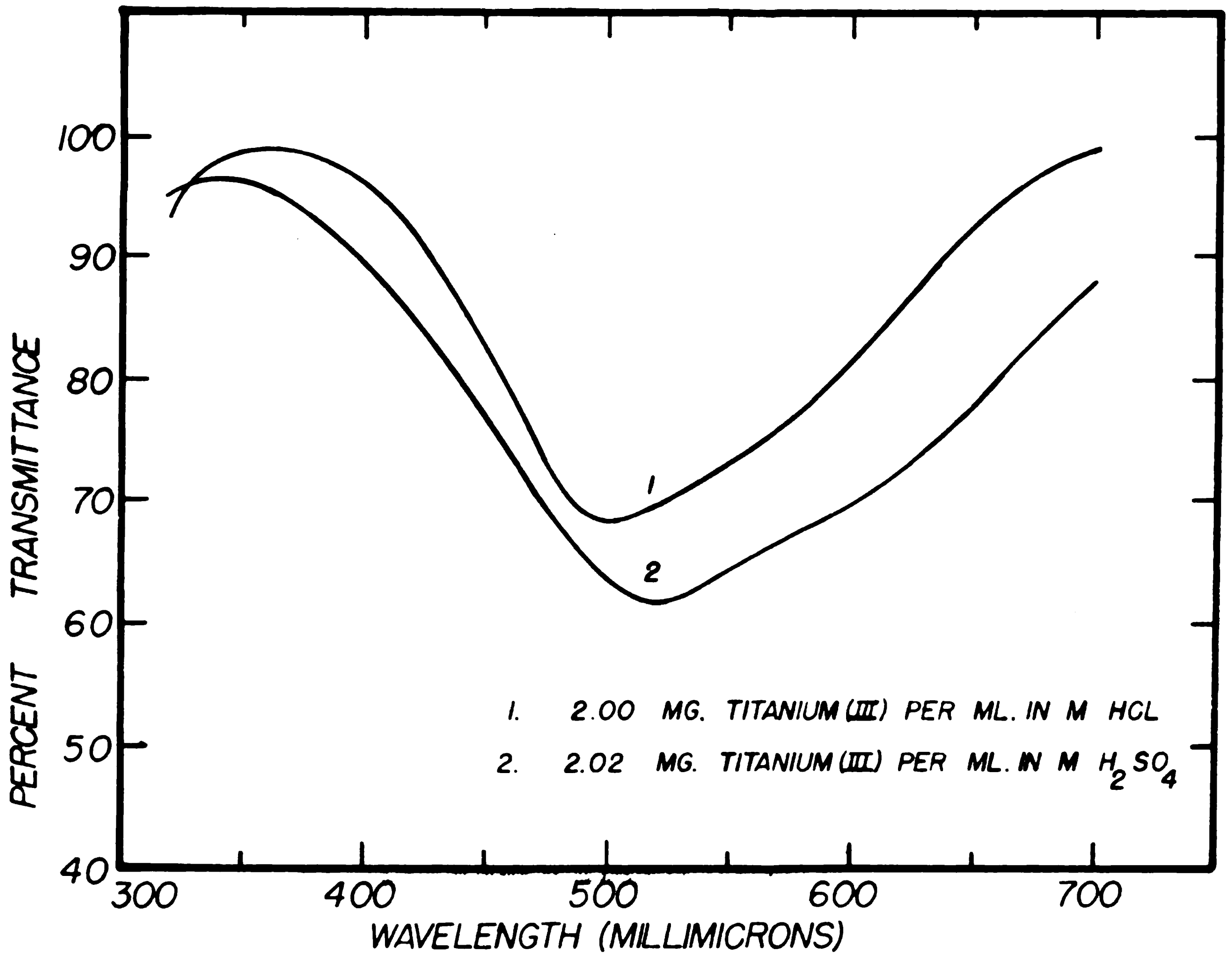
would of necessity have to be made immediately after dissolving and diluting the sample, and before any appreciable air-oxidation can occur.

To this end several samples of varying amounts of titanium were dissolved, and measurements at 520 millimicrons made immediately after dilution. At the same time, a volumetric determination of their titanous content was also made. As illustrated in Graph II, plotted on semi-log paper, the graphing of transmittancy on the abscissa vs. concentration on the ordinate results in very nearly a straight line, indicating the adherence to Beer's Law of the titanous solutions over the range of concentration studied. The solvent in each case was 1 M sulfuric acid.

A hydrochloric acid solution of titanous chloride was also prepared and studied in a manner similar to the titanous sulfate solution. The solvent was 1 M hydrochloric acid. As shown in Graph III a solution of titanous chloride having about the same concentration as one of titanous sulfate, differs appreciably from it in transmittancy. The distinctions may be seen in the ultra-violet region, at the point of minimum transmittancy,



GRAPH II. RELATIONSHIP BETWEEN TRANSMITTANCE AND CONCENTRATION OF TITANIUM (III) SOLUTIONS IN M H_2SO_4. MEASURED AT 520 MILLIMICRONS.



GRAPH III. EFFECT OF ANION ON TRANSMITTANCE OF TITANIUM (III) SOLUTION and in the red regions. A titanous chloride solution transmits considerably more in the red portion of the spectrum than does a titanous sulfate solution, a fact which is apparent even to the eye.

The transmittancy minimum of the titanous chloride solution has shifted to 505 millimicrons, from its position of 520 millimicrons for a titanous sulfate solution.

A titanous chloride solution, as distinguished from a titanous sulfate solution, exhibits an increase in transmittancy for a corresponding decrease in titanous concentration. This fact is shown in Table XI.

TABLE XI

COMPARISON OF TRANSMITTANCY AND TITANOUS CONTENT OF A TITANOUS CHLORIDE SOLUTION

Time (hrs)	Transmittancy	Mg. Ti per Ml.
0	69.5	1.99
23	69.5	1.95
46.5	70.6	1.86
71	72.8	1.72
95	75.1	1.48

It would have been profitable to carry out further studies in different acids. However, when it was attempted to dissolve titanium in perchloric acid, it was discovered that the metal was insoluble, even in solutions approaching 50 percent concentrated perchloric acid.

Attempts to dissolve the metal in phosphoric acid also proved fruitless, as the action was extremely slow. A sample dissolved in either sulfuric or hydrochloric acid to which was added some phosphoric acid also was shown to be unfeasible because of the precipitation of titanic phosphate, caused by air-oxidation. This precipitate formed on the surface of the solution in the Corex cells, and drifted down past the cell windows, making the reading erratic and unreliable.

An attempt was made to transfer quickly the solution to the cell in an atmosphere of carbon dioxide; benzene was then allowed to float on top of the titanous solution to protect it from the air. This too proved unsuccessful, because the titanous solution crept up the sides of the cell from underneath the benzene, again resulting in air oxidation and consequent precipitation of titanic phosphate.

The best solvent for metallic titanium is hydrofluoric acid. Even in dilute hydrofluoric acid, the dissolving is accompanied by the liberation of heat, and proceeds very rapidly. The resulting titanous solution is green, which upon air-oxidation becomes colorless.

CONCLUSIONS

CONCLUSIONS

Metallic titanium dissolves in hydrochloric or sulfuric acid to quantitatively form titanium (III). The titanous solution is very sensitive to air oxidation, and in order for it to remain in the trivalent state, oxygen must be excluded from the apparatus. This is easily accomplished by protecting the solution with an inert atmosphere of carbon dioxide or nitrogen.

The volumetric determination of the purity of a sample of titanium metal is thus greatly simplified, since no preliminary reduction of titanium (IV) is necessary.

The presence of phosphoric acid in the solution hastens the dissolving of titanium metal. Although phosphate forms a precipitate with titanium (IV), the precipitate does not constitute an interference with the subsequent titration.

Titanium (III) is determined by oxidation with ferric chloride and titration of the equivalent amount of iron (II) with dichromate or cerate.

Standard reducing solutions of titanium (III) may be made by dissolving a weighed sample of titanium of known purity in a Pyrex volumetric flask and diluting to volume. Titanous solutions in hydrochloric acid are more stable than those in sulfuric acid. However, even the former can not be used with an accuracy of greater than about ten parts per thousand.

Spectrophotometric studies of titanous solutions showed that the anion present in a given solution exerted an appreciable effect upon the transmitting curve. In a hydrochloric acid solution titanium (III) had a point of minimum transmittancy at 505 millimicrons; in sulfuric acid solution the minimum transmittancy occurred at 520 millimicrons.

A decrease of the content of titanium (III) in sulfuric acid solution is not accompanied by an increase in the transmittancy of the solution. In the case of titanous solutions in hydrochloric acid, the expected situation prevails, and a decrease of titanium (III) content is accompanied by an increase in the transmittancy of the solution. Measurements leading to this conclusion were made at 520 millimicrons.

Titanous solutions in sulfuric acid adhere to Beer's Law. However, the color of these solutions is not very intense, and the procedure would not be practical for solutions containing less than one milligram of titanium (III) per milliliter. Another point to be remembered is that colorimetric measurements must be made immediately after diluting the sample to volume. Nevertheless, the color of titanium (III) may be used as the basis of a colorimetric determination of titanium.

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TITANOUS SOLUTIONS FROM METALLIC TITANIUM

By

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AN ABSTRACT

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THESIS ABSTRACT

Titanium metal dissolved in hydrochloric or sulfuric acid was found to be quantitatively present as titanium (III), provided that the solution was protected from air oxidation with an inert atmosphere of carbon dioxide or nitrogen.

This fact provides a simple method for the determination of the purity of titanium metal, as the necessity of making a prior reduction of titanium (IV) is eliminated.

The dissolving of titanium metal was hastened by the addition of phosphoric acid to the acid solvent.

The titanium (III) content of the solution was conveniently determined by oxidation with ferric chloride, and titration of the equivalent amount of iron (II) with dichromate or cerate. There is a precipitation of titanic phosphate in solutions containing phosphoric acid, but this does not interfere with the titration.

Titanous chloride solutions show greater resistance to air oxidation than do titanous sulfate solutions. However, reducing solutions of titanous chloride made by dissolving a weighed amount of titanium of known purity in a Pyrex volumetric flask are not accurate to a degree of greater than one percent.

Spectrophotometric studies of titanous solutions indicate that the anion present in the solution exerts a considerable effect upon the point of minimum transmission. A titanous chloride solution transmits least at

a wave length of 505 millimicrons; a titanous sulfate solution at 520 millimicrons. The former also transmits more in the red region of the spectrum.

A decrease in titanium (III) concentration in sulfuric acid solution over a period of time does not cause a corresponding increase in transmittancy. In fact, the reverse is true. However, a hydrochloric acid solution decreasing in titanium (III) concentration does exhibit an increasing transmittancy.

The color of titanous solution is the basis of a colorimetric determination of titanium, since titanous sulfate solutions adhere to Beer's Law over the range of concentration studied. However, the color is not intense enough to serve for determining very small amounts of titanium. Measurements must be made immediately after dissolving and diluting the sample.