

# METHODS FOR ANALYSIS OF TITANIUM ALLOYS

## Colorimetric Determination of Silicon in Titanium Alloys

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The production of titanium metal and its alloys has increased rapidly in recent years. The intensive research which is being conducted on the metallurgical development of titanium alloys requires dependable analytical procedures, as does production control. Methods are proposed for determining silicon, calcium, aluminum, molybdenum, phosphorus, and boron in titanium alloys. Silicon is determined colorimetrically by the molybdenum blue method after most of the titanium has been hydrolyzed as a crystalline precipitate from a fluoboric acid solution by means of a new technique. The method is applicable to 0.005 to 1.5% silicon. In determining calcium, the titanium is separated from the calcium by cupferron precipitation and a chloroform extraction. The calcium is precipitated as calcium sulfate from a methanol medium, and the calcium weighed as calcium sulfate or determined nephelometrically as calcium stearate. The method is applicable to 0.005 to 0.3% calcium. In determining aluminum a cupferron precipitation is made on an 0.02-gram aliquot and the solution is filtered. The cupferron in the filtrate is destroyed by fuming with perchloric acid, the perchloric acid driven off, and the aluminum determined colorimetrically with aluminon. The method is applicable to 0.01 to 0.4% aluminum. A method is proposed for determining 0.25 to 10% molybdenum in molybdenum-titanium

alloys by precipitation as the sulfide from a hydrofluoric-sulfuric acid medium. In developing the procedure an exhaustive investigation was made of the factors involved in obtaining quantitative precipitation of molybdenum sulfide. A polarographic method is proposed for determining molybdenum in titanium alloys that is applicable to the range of 0.003 to 5% molybdenum. In this method the molybdenum is extracted with ether from a hydrochloric-sulfuric acid solution, the ether evaporated off, and the molybdenum determined polarographically from a perchloric acid medium. The conditions for obtaining quantitative extraction of the molybdenum were investigated. Phosphorus is determined colorimetrically by the molybdenum blue method after dissolving the sample in a mixture of hydrofluoric and nitric acids, evaporating to fumes of sulfuric acid, and complexing the titanium with sodium fluoride. The range of the method for phosphorus is 0.005 to 0.50%. In the method for boron the sample is dissolved in sulfuric acid, and the titanium and boron are oxidized with hydrogen peroxide. The peroxide is destroyed by boiling in the presence of an iron salt as a catalyst. The boron is distilled as methyl borate and the boron determined colorimetrically with dianthramide. The method is applicable to 0.0004 to 0.10% boron.

THE accurate determination of silicon in titanium alloys is a difficult matter. Dehydration with hydrochloric, perchloric, or nitric acid leaves a mass of titanium oxide which does not dissolve. A method has been proposed (31) for the determination of silicon in titanium alloys, in which sulfuric acid is used as the dehydrating agent. The sample is dissolved in sulfuric acid, hydrogen peroxide is added, and the solution is evaporated to fumes of sulfuric acid. The method is not applicable to alloys containing less than 0.1% silicon (31). Even with alloys containing more than 0.1% silicon the results may at times be erratic, because of the difficulty of converting occluded titanium sulfate to titanium oxide even at a temperature of 1000° C.

In view of the difficulties with the gravimetric methods for the determination of silicon in titanium alloys, it was decided to investigate the possible application of colorimetric procedures. There are two colorimetric procedures for silicon, the silicomolybdate method and the molybdenum blue method. The silicomolybdate method (2, 4, 11, 14, 18-20, 22, 27, 29) was considered but was abandoned because of its lack of sensitivity. The sensitive molybdenum blue method using 1-amino-2-naphthol-4-sulfonic acid and a mixture of sulfite and bisulfite as the reducing agent (5, 9, 10, 13, 25, 28) showed the most promise. The molybdenum blue method has been applied to the determination of silicon in aluminum (7, 10, 13), zirconium (10), beryllium (10), calcium (10), steels (12, 16), steam condensates (9, 28), magnesium alloys (1, 6), water (21), limestone (30), aluminous materials (7), biological materials (17), boiler scale (24), leach liquor (25), hydrofluoric acid (8), and cathode nickel (after a prior separation of the silica by dehydration) (26). None of the above methods is

applicable to the determination of silicon in titanium alloys. Carlson and Banks (10), for instance, state that their method for the determination of silicon in zirconium, beryllium, aluminum, and calcium will tolerate only 10 p.p.m. of titanium.

In the method proposed in this paper the titanium alloy is dissolved in hydrofluoric acid, and boric acid is added to complex the fluoride ion, as has been suggested by Kurtz (23), Case (11), and Carlson and Banks (10). Potassium permanganate is then added to oxidize the titanium, and the solution is heated in a boiling water bath for 90 minutes to hydrolyze the titanium and destroy the permanganate color. The solution is filtered and ammonium molybdate is added to form the yellow silicomolybdate color. Tartaric acid is then added to prevent interference from moderate amounts of phosphate (3, 9, 27) and to stabilize the silicomolybdate color (10). The molybdenum blue color is formed by the addition of a mixture of 1-amino-2-naphthol-4-sulfonic acid, sodium sulfite, and sodium bisulfite.

For dissolving the samples a mixture of hydrofluoric and sulfuric acids and a mixture of hydrofluoric and hydrochloric acids were tried, but the results were not very satisfactory even with adjustment of the pH with a pH meter prior to the addition of the molybdate. The use of hydrofluoric acid to dissolve the samples gave good results. When hydrofluoric acid was used to dissolve the samples, the pH prior to the addition of the ammonium molybdate was 1.5. It is necessary that the titanium be oxidized to the titanate state in order to obtain satisfactory results. Various oxidizing agents were tried, but only permanganate gave consistently good results. The permanganate will also oxidize any unreacted silane (15). In the hydrolysis of the titanium the solu-

tion must be heated 90 minutes in the boiling water bath. If a shorter heating time is used, the solutions may be cloudy after filtration. As the hydrolyzed titanium is crystalline and the silicon is tied up in a stable complex, no silicon is occluded by the precipitate. The molybdenum blue color is read at 700 instead of at 830  $m\mu$  (the point of maximum absorption) in order to obtain a better range. The color is read from 30 to 60 minutes after the addition of the reducing mixture. About 90 minutes after the addition of the reducing mixture the color begins to deepen slowly.

The purest reagents should be used in the method in order to reduce the color of the reagent blank. It was found that some lots of boric acid and ammonium molybdate contained significant amounts of silicon.

The method is designed for titanium alloys containing 0.005 to 1.5% silicon.

#### APPARATUS AND REAGENTS

Coleman Universal spectrophotometer, Model 14, with  $13 \times 105$  mm. cuvettes and a 14-215 (PC-5) filter.

Polyethylene bottles, Baker and Adamson hydrofluoric acid bottles with screw tops removed.

Parafilm (Marathon Corp., Menasha, Wis.).

Boric acid, reagent grade.

Boric Acid Solution, 4%. Add 40 grams of boric acid to about 800 ml. of water contained in a 1-liter volumetric flask. Warm to about 40° C. to dissolve. Cool and dilute to 1 liter with water.

Dilute Hydrofluoric Acid, 3 to 7. Dilute 150 ml. of hydrofluoric acid (50%) to 500 ml. with water in a Bakelite graduate. Store in a regular hydrofluoric acid bottle.

Potassium Permanganate Solution, 3%. Dissolve 15 grams of potassium permanganate, reagent grade, in water and dilute to 500 ml. with water.

Ammonium Molybdate Solution, 5%. Dissolve 25 grams of ammonium molybdate, reagent grade, in water and dilute to 500 ml. with water.

Tartaric Acid Solution, 20%. Dissolve 100 grams of tartaric acid, reagent grade, in water and dilute to 500 ml. with water.

Reducing Solution. Dissolve 30 grams of sodium bisulfite, reagent grade, 1 gram of anhydrous sodium sulfite, reagent grade, and 0.5 gram of 1-amino-2-naphthol-4-sulfonic acid (Eastman Kodak) in about 175 ml. of water and dilute to 200 ml. with water. Filter through a medium filter paper (Whatman No. 40). Store in a polyethylene bottle. Make fresh weekly.

Standard Silicon Solutions 1 and 2. Three 1.0000-gram portions of sodium metasilicate,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , were weighed into beakers. Water and sulfuric acid were added and the silicon was dehydrated in the regular manner; 1.0000 gram of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  was found to contain 0.09706 gram of silicon (theoretical amount was 0.09873 gram). Standard silicon solution 1 was prepared by dissolving 1.0303 grams of sodium metasilicate in water and diluting to 2 liters in a volumetric flask. This solution contained 0.05 mg. of silicon per ml. Standard silicon solution 2 was prepared by dissolving 5.1515 grams of sodium metasilicate in water and diluting to 1 liter in a volumetric flask. Each milliliter of this solution contained 0.5 mg. of silicon. Both standard silicon solutions were stored in wax-lined glass bottles.

#### PROCEDURE

**Procedure for Samples Containing Less than 0.18% Silicon.**  
**PREPARATION OF CALIBRATION CURVE.** Transfer varying amounts of standard silicon solution 1 to polyethylene bottles. Add 40 ml. of water and 5 ml. of hydrofluoric acid (3 to 7) measured with a Bakelite graduate. Add 100 ml. of 4% boric acid solution. Transfer to 250-ml. volumetric flasks. Within 1 hour add 10.0 ml. of 5% ammonium molybdate solution and swirl. Allow to stand 10 minutes to develop the silicomolybdate color. Add 5.0 ml. of 20% tartaric acid solution and swirl. Immediately add 3.0 ml. of reducing solution and swirl. Dilute to the 250-ml. mark with water and mix. Within 30 to 60 minutes compare colorimetrically with the blank at 700  $m\mu$ . Make a calibration curve by plotting the per cent silicon against per cent transmittance. The calibration curve obtained by the authors followed Beer's law.

**METHOD.** Transfer 0.5 gram of the sample to a polyethylene bottle and add 40 ml. of water and 5 ml. of dilute hydrofluoric acid (3 to 7) measured with a Bakelite graduate. Cover the bottle with a piece of Parafilm, and allow the sample to dissolve by standing overnight without heating. Add 100 ml. of water and 4.0 grams of boric acid and swirl to dissolve the boric acid. Add 3% potassium permanganate solution with a medicine dropper until the solution in the polyethylene bottle is pink, and

then add 5 drops in excess. Rinse down the top and side of the polyethylene bottle to remove any adhering potassium permanganate solution. Place the polyethylene bottle in a 1-liter beaker containing about 800 ml. of boiling water. Place the beaker on the hot plate so that its lip faces toward the center of the hot plate. Allow the polyethylene bottle to rest in the groove of the beaker lip. If the beaker were placed with its lip facing toward the edge of the hot plate, superheating of the lip would cause a hole to be melted in the side of the bottle. Keep the bottle in the boiling water bath for 90 minutes. Swirl occasionally during the heating. Remove the bottle from the beaker and cool to room temperature. Filter through a fine filter paper (Whatman No. 42) into a 250-ml. volumetric flask. Wash the bottle and filter paper with water. Dilute the filtrate to about 200 ml. with water. Within 1 hour add 10.0 ml. of 5% ammonium molybdate solution and swirl. Allow to stand 10 minutes to develop the yellow silicomolybdate color. Add 5.0 ml. of 20% tartaric acid solution and swirl. Immediately add 3.0 ml. of reducing solution and swirl. Dilute to the 250-ml. mark with water and mix. Within 30 to 60 minutes compare colorimetrically with the blank at 700  $m\mu$ . Convert the readings to per cent silicon by consulting the calibration curve.

**Procedure for Samples Containing 0.18 to 1.5% Silicon.**  
**PREPARATION OF CALIBRATION CURVE.** Transfer varying amounts of standard silicon solutions 1 and 2 to polyethylene bottles. Add 40 ml. of water and 5 ml. of hydrofluoric acid (3 to 7) measured with a Bakelite graduate. Add 100 ml. of 4% boric acid solution. Transfer to 250-ml. volumetric flasks and dilute to the mark with water. Pipet 25-ml. aliquots into 250-ml. volumetric flasks. Dilute to about 200 ml. with water. Add the reagents, develop the color, and proceed as described for the preparation of the calibration curve for samples containing less than 0.18% silicon.

**METHOD.** Proceed as for samples containing less than 0.18% silicon to the point at which the solution has been filtered into the 250-ml. volumetric flask following the hydrolysis of the titanium. Dilute to the 250-ml. mark with water. Pipet a 25-ml. aliquot into a 250-ml. volumetric flask and dilute to about 200 ml. with water. Add the reagents, develop the color, and proceed as for samples containing less than 0.18% silicon. Convert the readings to per cent silicon by consulting the calibration curve.

#### RESULTS AND DISCUSSION

The method was checked by adding standard silicon solution to iodide titanium and carrying the samples through the procedure (Table I).

No satisfactory titanium alloy containing small amounts of silicon was available. However, this laboratory had on hand a titanium alloy containing about 1% silicon. This sample was run seven times by the sulfuric acid dehydration method (31) and seven times by the colorimetric method (Table II). It is seen

Table I. Silicon in Titanium Alloys by Colorimetric Method

| Silicon Added, % | Average Silicon Found, % | Standard Deviation, % | No. of Dets. |
|------------------|--------------------------|-----------------------|--------------|
| 0.005            | 0.007                    | 0.0011                | 5            |
| 0.010            | 0.011                    | 0.0022                | 5            |
| 0.020            | 0.023                    | 0.0018                | 5            |
| 0.030            | 0.030                    | 0.0016                | 5            |
| 0.100            | 0.100                    | 0.0021                | 5            |
| 0.140            | 0.142                    | 0.0030                | 5            |
| 0.180            | 0.180                    | 0.0058                | 5            |
| 0.20             | 0.21                     | 0.017                 | 6            |
| 0.40             | 0.40                     | 0.019                 | 5            |
| 0.60             | 0.59                     | 0.021                 | 5            |
| 1.00             | 1.03                     | 0.039                 | 8            |
| 1.50             | 1.50                     | 0.078                 | 8            |

Table II. Comparison of Silicon Results by Gravimetric and Colorimetric Methods

|                    | Gravimetric Results, % | Colorimetric Results, % |
|--------------------|------------------------|-------------------------|
|                    | 1.11                   | 1.12                    |
|                    | 1.10                   | 1.13                    |
|                    | 1.16                   | 1.13                    |
|                    | 1.13                   | 1.22                    |
|                    | 1.08                   | 1.15                    |
|                    | 1.07                   | 1.13                    |
|                    | 1.17                   | 1.15                    |
| Average            | 1.117                  | 1.147                   |
| Standard deviation | 0.038                  | 0.034                   |

that the two methods check within 0.03%. The precision of the colorimetric method is somewhat better than the precision of the gravimetric method.

There is no danger of silicon occurring in commercial titanium alloys as elemental silicon because of the high temperatures used in making titanium alloys and the great solubility of silicon in titanium. Titanium will dissolve up to 8.5% silicon without the formation of elemental silicon. The fact that silicon is not present as elemental silicon in titanium alloys is an important point, as elemental silicon is not very soluble in hydrofluoric acid. Aluminum alloys frequently contain elemental silicon, because silicon has only a limited solubility in aluminum. No trouble was encountered in dissolving titanium alloys in the dilute hydrofluoric acid used. Most titanium alloys dissolve within 3 hours. However, the safe procedure is to allow the samples to dissolve overnight.

Interferences that might be present in titanium alloys were studied. The amounts of the elements that did not interfere (in the presence of 0.5 gram of titanium) are shown in Table III. The presence of more than 7.5% iron or more than 10% chromium leads to low results, probably because some of the reducing agent is used to reduce the ferric ion partially to the ferrous state and the chromic ion to the chromous state. Low results were obtained when more than 0.75% copper was present. This could be due to the use of the reducing agent to reduce the cupric ion to the cuprous state. However, the interference of this relatively small amount of copper could be due to some negative catalytic effect. Any copper present in a titanium alloy is reduced to the metallic state by the titanous ion when the sample is dissolved. This metallic copper is subsequently dissolved on heating the solution with permanganate. The presence of more than 2.5% nickel or 2.5% cobalt leads to low results for silicon. More than 0.5% phosphorus gives high results for silicon. All the above limits for interferences in titanium alloys are greater than the nominal amounts of these elements that would be found in commercial titanium alloys.

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**Table III. Amounts of Alloying Elements Not Interfering with Colorimetric Determination of Silicon in Titanium Alloys**

| Element    | Added as                                                                           | Amount That Did Not Interfere, %  |
|------------|------------------------------------------------------------------------------------|-----------------------------------|
| Iron       | FeSO <sub>4</sub> ·7H <sub>2</sub> O                                               | 7.5 (maximum amount permissible)  |
| Chromium   | (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> <sup>a</sup>        | 10 (maximum amount permissible)   |
| Copper     | CuSO <sub>4</sub> ·5H <sub>2</sub> O                                               | 0.75 (maximum amount permissible) |
| Nickel     | NiCl <sub>2</sub> ·6H <sub>2</sub> O                                               | 2.5 (maximum amount permissible)  |
| Cobalt     | CoCl <sub>2</sub> ·6H <sub>2</sub> O                                               | 2.5 (maximum amount permissible)  |
| Phosphorus | (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>                                   | 0.5 (maximum amount permissible)  |
| Aluminum   | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O                | 5                                 |
| Manganese  | MnSO <sub>4</sub> ·H <sub>2</sub> O                                                | 10                                |
| Vanadium   | (VO) <sub>2</sub> Cl <sub>4</sub>                                                  | 5                                 |
| Calcium    | CaCl <sub>2</sub> ·2H <sub>2</sub> O                                               | 5                                 |
| Molybdenum | (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O | 10                                |
| Boron      | H <sub>2</sub> BO <sub>3</sub>                                                     | 1                                 |
| Tungsten   | Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O                                 | 5                                 |
| Tin        | SnCl <sub>2</sub> ·2H <sub>2</sub> O                                               | 5                                 |
| Carbon     | Titanium alloy containing 0.5% carbon                                              | 0.5                               |

<sup>a</sup> Chromate ion is reduced to chromic state in dissolving titanium metal.

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## (Methods for Analysis of Titanium Alloys)

# Nephelometric and Gravimetric Determination of Small Amounts of Calcium in Titanium Alloys

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CALCIUM is sometimes present as an impurity in titanium alloys. Hitherto, no methods have been published for the determination of calcium in this type of alloy. The usual methods for the determination of calcium are not directly applicable to titanium alloys.

The classical oxalate method (8, 14, 26), whereby the calcium is precipitated as the oxalate from a slightly ammoniacal solution containing a moderate excess of oxalate, is not applicable to titanium alloys because of the coprecipitation of titanium. The precipitation of calcium oxalate from a slightly acidic solution (15) will provide a separation of calcium from small but not large

amounts of titanium. The use of a very large excess of oxalate ion will complex the titanium and prevent its precipitation from either an ammoniacal solution or an acidic solution. However, under these conditions the precipitation of the calcium oxalate is very incomplete.

The separation of calcium as the sulfate from an alcoholic medium (1, 9) is not directly applicable to titanium alloys. It was found that with a solution containing titanium sulfate, calcium sulfate, and alcohol no precipitate at all could be obtained, probably because of the formation of a titanium-calcium complex. The precipitation of the calcium as calcium molybdate