

NRL Report 7182

Procedures for the Analysis of Metals, Alloys, and Other Materials of Research

Part 6 - Procedures for Preparation of Sample Solutions in Oxalic Acid for Spectrophotometric Determination of Titanium

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PREVIOUS REPORTS IN THIS SERIES

"Part 1 – Procedures for the Chemical Analysis of Copper-Base Alloys,"
O. R. Gates and O. Mylting, NRL Report 6357, Mar. 1966

"Part 2 – Determination of Silver and Indium in Magnesium-Base Alloys,
Lead in Indium, and Zirconium in Hafnium," O. R. Gates and E. J. Brooks,
NRL Report 6427, Sept. 1966

"Part 3 – A Spectrophotometric Procedure for the Determination of Trace
Amounts of Cobalt in Ferrous Alloys," O. R. Gates, NRL Report 6857, Dec.
1968

"Part 4 – Spectrophotometric Procedures for the Determination of Ions Formed
Within Stress," O. R. Gates, NRL Report 6948, Oct. 1969

"Part 5 – An Investigation of the Chemical Analysis of Cadmium-Zinc Arse-
nide," O. R. Gates and R. W. Black, NRL Report 7146, Sept. 1970

ABSTRACT

The chemical analysis of titanium is complicated by the tendency of its ions to hydrolyze in neutral or slightly acidic solutions. However, in 0.3M oxalic acid, the titanium solutions remain stable and clear because hydrolysis of titanium is prevented. Therefore, sample solutions of various inorganic ions were prepared in oxalic acid to determine titanium. Aliquots of the sample solutions can be taken for the spectrophotometric determination of 0.004% to 10.0% titanium with tiron. The exclusion of fluoride reagents eliminates a source of color interference and a health hazard.

PROBLEM STATUS

This is the sixth in a series of progress reports; work on the problem is continuing.

AUTHORIZATION

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PROCEDURES FOR THE ANALYSIS OF METALS, ALLOYS, AND OTHER MATERIALS OF RESEARCH

Part 6 -- Procedures for Preparation of Sample Solutions in Oxalic Acid for Spectrophotometric Determination of Titanium

INTRODUCTION

This is the sixth in a series of reports which describe progress in analytical methods by the Analytical Chemistry Branch of the Central Materials Research Activity.

The chemical analysis of titanium is complicated by the tendency of its ions to hydrolyze in neutral or slightly acidic solutions (1a). The hydrolytic precipitation of metatitanic acid is especially troublesome in color-dependent procedures (2,3). Prevention of hydrolysis, therefore, would simplify and facilitate spectrophotometric determinations of titanium.

PREPARATION OF SAMPLE SOLUTIONS

Scope

Digestion and fusion procedures are adapted for solubilization of total amounts of titanium in 0.1- to 0.5-g samples of metals, alloys, ores, and ceramic materials. The digestates and melts are dissolved, filtered, and brought to volume in 0.3M oxalic acid. From 0.004% to 10.0% titanium can be determined spectrophotometrically on aliquots of the prepared solutions, which remain stable and free of precipitates.

Apparatus

Bottles -- Glass, 4-oz capacity, narrow mouth, with plastic screw caps.

Burner -- Fisher-type, with 40-mm grid, for use with natural gas.

Crucibles -- Fused silica, 50-ml capacity.

Crucibles -- Platinum, 40-ml capacity.

Filters -- Millipore, MF type HA, 25-mm disk, 0.45- μ pore size.

Filter bell -- Pyrex glass, 10-cm inside diameter, 20-cm inside height, with bottom ring of rubber, and brass slide valve, obtained from New York Laboratory Supply Co., Inc. (The filter-bell is set, by preference, on a glass plate.)

Filter holder -- Microanalysis, Pyrex glass, for vacuum filtrations with 25-mm Millipore filter disks, obtained from Millipore Corporation. (The filter holder is fitted in the filter bell through a rubber stopper.)

Furnace -- Muffle, electric, "Multiple Unit" manufactured by the Hevi Duty Electric Co.

Reagents

Analytical-grade reagents, as received, are used in the preparation of reagent solutions.

Carbon Dioxide – Commercial-grade CO_2 (99.5% CO_2) is used directly from a 9-by-52-inch cylinder.

Hydrochloric Acid (1:1 Solution) – Concentrated HCl (250 ml) is mixed with 250 ml of H_2O .

Hydrogen Peroxide (30% Solution) – Hydrogen peroxide (assay 30% to 32% H_2O_2) is used as received.

Oxalic Acid (0.3M Solution) – Oxalic acid dihydrate (75.64 g) is dissolved in 1500 ml of H_2O and diluted to 2000 ml.

Sodium Carbonate – Anhydrous granular sodium carbonate is used as received.

Digestion Procedure

Materials such as cast iron and steel, in chip form, are brought into solution by digestion as follows: A 0.1000-g sample is transferred to a 100-ml beaker. By pipet, 10 ml of 1:1 HCl is added, and the resulting solution is digested at 80° to 90°C on a hot plate for 1 hour. After the contents are cooled to room temperature, 5 ml of 30% H_2O_2 is carefully pipetted into the beaker and allowed to stand for 1 hour. Moderate effervescence may follow this treatment. The mixture is digested on a hot plate for a second time until effervescence ceases (approximately 10 min). After the cover and walls of the beaker are rinsed, the digestate is evaporated to dryness.

The residue is treated with 25 ml of 0.3M oxalic acid, stirred occasionally, and allowed to dissolve at room temperature for 30 min. Then, 5 ml of concentrated HCl is added and the solution is filtered by partial vacuum through a 25-mm Millipore HA disk directly into a 100-ml volumetric flask under a bell jar. The residue is washed and the filtrate is diluted to 100 ml with 0.3M oxalic acid, only. The solution is transferred to a 4-oz glass bottle fitted with a plastic screw cap.

Carbon dioxide from a cylinder is bubbled through a water trap and a glass tube to the bottom of the bottle of solution for 5 min. The prepared solution is stable in the ordinary light of the laboratory.

Fusion Procedure

Ores and refractory materials are rendered soluble by a fusion technique with sodium carbonate (1b) modified as follows: A 0.5000-g sample is mixed with 4.00 g of granular anhydrous sodium carbonate in a 40-ml platinum crucible. The crucible is placed upright and uncovered on a tripod, and the mixture is fused with a Fisher burner, gradually increasing the flame to maximum heat in the first 10 min and continuing at maximum heat for the next 20 min. The clear melt is cooled to room temperature.

Ten ml of H_2O is added by pipet to the crucible and warmed on a hot plate. The fusion cake is detached into a 150-ml beaker, and the crucible is rinsed with H_2O . To dissolve any adhering particles, 10 ml of concentrated HCl is pipetted into the crucible, warmed on a hot plate, and carefully (effervescence) transferred to the beaker. This treatment is repeated with a second 10 ml of HCl, and the crucible is rinsed with H_2O . The solution (approximately 60 ml) is evaporated nearly to dryness on a hot plate. The residue, which may contain silica, should have a distinct odor of HCl.

The dehydrate residue is drenched with 5 ml of concentrated HCl. Then 25 ml of 0.3M oxalic acid is added, and the mixture is dissolved on a hot plate for 20 min. The hot solution is filtered by partial vacuum through a 25-mm Millipore HA disk directly into a 100-ml volumetric flask under a bell jar. The residue is washed and the filtrate is diluted to volume with 0.3M oxalic acid, only. The prepared sample solution is stored in a 4-oz glass bottle fitted with a plastic screw cap. Solutions of high-iron samples should be treated with CO₂ as described in the digestion procedure.

Ignition of Metallic Samples

Titanium, niobium, and tantalum metals and titanium-niobium alloys are ignited in air to their oxides before fusion. Test samples weighing 0.2000 g, in fine-granular texture, or as 1-by-4-mm strips of 0.008-inch foil in the case of tantalum, are ignited in 50-ml fused silica crucibles in a muffle furnace at 800° to 850°C. The granular samples oxidize in 30 min, but the strips of foil require approximately 1 hour for complete oxidation.

The oxidized samples are fused either with sodium bisulfate (NaHSO₄, fused) or transferred to platinum crucibles and fused with sodium carbonate as described previously. The melts are dissolved in 100 ml of 0.6M oxalic acid at 70° to 80°C, cooled, and diluted with water to 200 ml. The prepared sample solutions are apparently stable indefinitely.

Titanium in the Sample Solutions

Titanium concentrations in the prepared solutions are determined by a spectrophotometric method (4) using tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate) as the sensitive chromogenic reagent. Depending on the sample weight and the aliquot taken, the method is suitable to determine 0.004% to 10.0% titanium in a wide variety of inorganic materials. However, titanium was not determined in the sample solutions of niobium and tantalum because of interfering color complexes.

DISCUSSION

Digestion Procedure

In early tests, samples were digested in dilute HCl alone. Results in Table 1 show that digestions in 1:2 HCl dissolved only partial amounts of the titanium in each of four NBS standard samples of cast iron and steel. Also, the relative percentages of titanium found in the cast irons were less than those obtained in the steels. In later tests, digestion in 1:1 HCl likewise dissolved only partial amounts of the titanium in the four standard samples.

Hydrogen peroxide was then tested as a supplemental solvent for the undissolved titanium in the HCl digestates. The additional digestion with dilute HCl and H₂O₂ together completely solubilized the titanium. As shown in Table 1, the amounts of titanium found agree closely with the NBS certified analyses. The most favorable results were obtained after digestions with 10 ml of 1:1 HCl and 5 ml of 30% H₂O₂.

Slight amounts of the test samples remained undissolved even after the second digestions. Under microscopic examination the residues from the cast iron samples appeared to be a mixture of graphite and silica particles. The residues from the steel samples had the appearance of silica particles. Since total amounts of titanium in the four samples were obtained by double digestions, solubilization of the final residues by fusion was not required.

Table 1
Effect of Digestion Treatment on Titanium Determination and
Stability of Sample Solutions of Cast Iron and Steel

Sample (0.1000 g)	Digestion Treatment	Titanium (%)		Stability of Sample Solution
		NBS Certificate	Found*	
Cast iron NBS No. 4i	20 ml 1:2 HCl	0.026	0.002	3 weeks
	20 ml 1:2 HCl + 1 ml H ₂ O ₂		0.024	6 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂		0.027	More than 3 years
	10 ml 1:1 HCl + 5 ml H ₂ O ₂ and deaeration with CO ₂ †			More than 3 years
Cast iron NBS No. 7g	20 ml 1:2 HCl	0.044	0.009	4 weeks
	20 ml 1:2 HCl + 1 ml H ₂ O ₂		0.036	6 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂		0.036	6 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂ and deaeration with CO ₂ †		0.044	More than 3 years
Steel, A.O.H. NBS No. 19g	20 ml 1:2 HCl	0.027	0.021	2 weeks
	20 ml 1:2 HCl + 1 ml H ₂ O ₂		0.032	5 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂		0.024	6 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂ and deaeration with CO ₂ †		0.027	More than 3 years
Steel, B.O.H. NBS No. 170a	20 ml 1:2 HCl	0.281	0.132	2 weeks
	20 ml 1:2 HCl + 1 ml H ₂ O ₂		0.285	5 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂		0.282	6 weeks
	10 ml 1:1 HCl + 5 ml H ₂ O ₂ and deaeration with CO ₂ †		0.279	More than 3 years

* Titanium was determined spectrophotometrically with tiron.

† Carbon dioxide gas was bubbled through the prepared sample solution for 5 min.

The dilute oxalic acid solutions of cast iron and steel developed yellow crystalline precipitates after standing a few weeks. These precipitates, probably ferrous oxalate (5), may have formed through the photochemical reduction of ferric iron in the solutions (6). Deaeration with CO₂, however, stabilized the solutions and prevented the development of these yellow crystals. The oxalic acid sample solutions of cast iron and steel which were initially gassed with CO₂ have remained clear and free of precipitates for more than 3 years.

Fusion Procedure

Experimental fusions of 0.1000-g samples with 4.00 g of potassium pyrosulfate produced melts which dissolved readily in 0.3M oxalic acid. Overnight, however, colorless crystals developed in the prepared solutions. Similar crystals also developed after melts of the potassium pyrosulfate flux alone were dissolved in the dilute oxalic acid. The crystals from both melts were identified as potassium tetraoxalate [$\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$] by x-ray analysis.

After comparable fusions with sodium bisulfate (NaHSO_4 , fused), the melts did not form corresponding crystals of sodium tetraoxalate when dissolved in dilute oxalic acid. Fusions with sodium bisulfate, however, solubilized only part of the titanium in NBS standard samples of bauxite, magnetite iron ore, alumina refractory, and burned magnesite. Total amounts of titanium in these reference materials were obtained, however, by the described fusion procedure with sodium carbonate (Table 2).

Table 2
Titanium Determination in NBS Standard Reference Materials
After Preparation of Samples in Oxalic Acid Solution

Material	NBS SRM No.	Weight of Sample Taken (g)	Titanium (%)		
			NBS Certificate*	After Preparation in Oxalic Acid†	Difference
Bauxite	69a	0.500	1.68	1.72	0.04
Magnetite iron ore	29a	0.100	0.09	0.09	0.00
Alumina refractory	76	0.100	1.32	1.31	-0.01
Burned magnesite	104	0.500	0.018	0.020	0.002
Feldspar	99	0.500	0.010	0.010	0.000
Flint clay	97	0.500	1.43	1.45	0.02
Glass sand	81	0.500	0.057	0.057	0.000

*Titanium values were calculated from NBS certificate values for TiO_2 .

†Titanium was determined spectrophotometrically with tiron.

Furthermore, it should be noted that the tendency of the sodium bisulfate flux to spatter when heated requires additional attention and time for fusions.

Prepared sample solutions of most ceramic and other low-iron materials remain free of ferrous oxalate precipitates. However, prepared solutions containing more than 0.1 g of iron in 100 ml of 0.3M oxalic acid should be deaerated with CO_2 to sustain lasting stability.

Fluorides

Hydrofluoric acid and fluoride salts were not introduced as reagents in any of the foregoing procedures for preparation of sample solutions. The exclusion of fluoride eliminates a source of serious interference in the formation of the colored titanium-tiron complex (7).

The exclusion of hydrofluoric acid also eliminates the health hazard of handling a highly toxic and corrosive liquid.

SUMMARY

Solubilization and dissolution procedures were developed for the preparation of sample solutions of various inorganic materials in 0.3M oxalic acid. In this dilute oxalic acid medium, the hydrolysis of titanium is prevented, and prepared solutions remain stable indefinitely. Precipitation of ferrous oxalate is prevented by bubbling CO₂ through sample solutions of high iron content. Aliquots of the prepared solutions are suitable for spectrophotometric determination of 0.004% to 10.0% titanium.

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