

# Titanium Determination with Disodium-1,2-Dihydroxybenzene-3,5-Disulfonate (Tiron) in Oxalic Acid Solution

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**A stable spectrophotometric method is presented for the determination of titanium with tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate). Preparation of samples in 0.3M oxalic acid prevents the hydrolytic precipitation of titanium; and sample solutions retain lasting stability. In test solutions at pH 5.2 to 5.6, the yellow titanium tiron complex remains color stable and free of turbidity. Absorbance measurements of the developed color at 420 nm permit determination of 2 to 100  $\mu\text{g}$  of titanium in 50-ml test solutions. Interference effects and tolerance limits for diverse metallic ions are reported. Iron(III) interference is prevented by reduction with sodium dithionite; copper is masked with thiourea; and chromium is eliminated by volatilization. More than 30  $\mu\text{g}$  of molybdenum and 25  $\mu\text{g}$  of niobium or tantalum interfere. The method is suitable for determination of 0.004 to 10.0% of titanium in metals, alloys, ores, and ceramic materials.**

TITANIUM DETERMINATIONS by available spectrophotometric methods lacked either the sensitivity or stability needed in recent metallurgical investigations. Conventional hydrogen peroxide methods possessed low sensitivity; and procedures using more sensitive reagents showed transient stabilities. Major interferences restricted applicability of the methods.

This report presents procedures developed for the preparation of stable sample solutions and the precise determination of titanium in dilute oxalic acid. Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate), first studied analytically by Yoe and Armstrong (1), serves as the sensitive chromogenic reagent.

## EXPERIMENTAL

**Apparatus.** For vacuum filtrations, a 25-mm i.d. micro-analysis filter holder (Millipore Corp.) was fitted through a rubber stopper in the top of a 20-cm (inside height) filter bell jar (New York Laboratory Supply Co.) which accommodates a 100-ml volumetric flask.

A Beckman Model G pH meter with micro electrodes was used to verify the pH of test solutions.

A Coleman Model 6A Junior spectrophotometer with 12  $\times$  75 mm (10-mm i.d.) round cuvettes was used to measure absorbances.

**Reagents.** Reagent solutions were prepared from analytical grade chemicals as received.

Ammonium citrate, dibasic, 1M. Dissolve 226.2 grams of  $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$  in water and dilute to 1 liter. The prepared solution should be water clear.

Disodium ethylenediaminetetraacetate, 0.1M. Dissolve 7.45 grams of  $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  in 150 ml of water and dilute to 200 ml.

Oxalic acid, 0.3M and 0.6M. Prepare solutions from crystals of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

Sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$ , powder. Add as a dry reagent.

Standard titanium solutions. Prepare 100 ml of stock solution containing 1 mg of Ti per ml by fusing 0.1674 gram of  $\text{TiO}_2$  (NBS Standard Reference Material No. 154a) with sodium carbonate as described under preparation of sample

solutions. Prepare solutions containing 10  $\mu\text{g}$  and 100  $\mu\text{g}$  of Ti per ml by pipetting 1 ml and 10 ml, respectively, of the stock solution into 50-ml volumes of 0.6M oxalic acid and diluting each with water to 100 ml.

Thiourea,  $\text{NH}_2\text{CSNH}_2$ , granular crystals, mp 174–176 °C. Add as a dry reagent.

Tiron,  $(\text{HO})_2\text{C}_6\text{H}_2(\text{SO}_3\text{Na})_2$ , 4%. Dissolve 4.00 grams of tiron in 50 ml of water and dilute to 100 ml. Store in a screw-capped bottle in a refrigerator at 5 °C. The prepared solution should be water clear. Reject any discolored solution.

Diverse ions. Prepare a 100-ml stock solution of each diverse ion from its chloride, oxide, or metal at a concentration of 1000  $\mu\text{g}$  of the ion per ml. Prepare a dilute solution containing 10  $\mu\text{g}$  of the diverse ion per ml from the stock solution.

**Preparation of Sample Solutions.** Soluble samples were decomposed by acid digestion. Refractory materials were solubilized by fusion attack.

Cast irons and steels were brought into solution by the following digestion procedure: Transfer 0.1000 gram of material to a 100-ml beaker. Add 10 ml of 1:1 hydrochloric acid and digest on a hot plate at 80 to 85 °C for 1 hour. Pipet 5 ml of 30% hydrogen peroxide into the beaker at room temperature and let stand for 1 hour. Digest at low heat until evolution of gas bubbles ceases (ca. 10 min), then evaporate to dryness.

Add 25 ml of 0.3M oxalic acid and let dissolve at room temperature for 30 min. Add 5 ml of concd hydrochloric acid, and, chiefly to remove silica and graphitic carbon, filter under partial vacuum through a 25-mm Millipore HA disk into a 100-ml volumetric flask. With 0.3M oxalic acid only, wash the residue and dilute the filtrate to 100 ml. Transfer the solution to a 4-oz. bottle fitted with a plastic screw cap. Bubble carbon dioxide into the cylinder through a water trap and a glass tube to the bottom of the bottle of solution for 5 minutes.

Fusion with sodium carbonate was used to decompose ceramic materials and ores as follows: Mix 0.5000 gram of sample with 4.00 grams of sodium carbonate in a 40-ml platinum crucible. Fuse the mixture for 30 min upright and uncovered above a Fisher burner, gradually increasing the flame to maximum heat during the first 10 min. When cool, add 10 ml of water to the crucible, warm and detach the fusion cake into a 150-ml beaker. Pipet 10 ml of concd HCl into the crucible, warm and transfer the acid to the beaker. Repeat this HCl treatment, and rinse the crucible with water. Evaporate the solution (ca. 60 ml) to dryness.

Drench the dehydrated residue with 5 ml of concd HCl. Add 25 ml of 0.3M oxalic acid, and dissolve on a hot plate for 20 min. While hot, filter (mainly silica) under partial vacuum through a 25-mm Millipore HA disk. With 0.3M oxalic acid only, wash the residue and dilute the solution to 100 ml. Store the sample solution in a 4-oz. screw-capped bottle. Prepared solutions of high-iron samples should be treated with carbon dioxide as described under the digestion procedure.

**Spectrophotometric Procedure.** Pipet a 10-ml or smaller aliquot containing 0 to 100  $\mu\text{g}$  of titanium into a 50-ml beaker. (If the smaller aliquot is taken, add 0.3M oxalic acid to bring the volume to 10 ml.) Add 5 ml of 0.1M disodium EDTA solution and 10 ml of 1M ammonium citrate. With

(1) J. H. Yoe and A. R. Armstrong, *ANAL. CHEM.*, **19**, 100 (1947).

a small piece of Congo red paper as indicator in the solution, add concd ammonium hydroxide dropwise until the paper becomes final bright red. Then add 1 more drop of  $\text{NH}_4\text{OH}$ . The solution should now have a pH of 5.2 to 5.6 as verified by a pH meter.

Transfer 200 mg of sodium dithionite powder into the beaker, stir thoroughly, and let stand uncovered for 10 min. Add 1.0 g of thiourea granular crystals, stir until dissolved, and let stand open for 10 min. Pipet 5 ml of 4% tiron solution into the beaker, stir, and let stand uncovered for 10 min. Transfer the colored solution to a 50-ml volumetric flask, dilute to capacity with water, and let stand for 20 min.

Measure the absorbance at a wavelength of 420 nm using water as the reference liquid. Determine the titanium concentration from a calibration curve prepared from the absorbances of a series of solutions containing 0 to 100  $\mu\text{g}$  of standard titanium.

## RESULTS AND DISCUSSION

**Preparation of Samples.** Digestion in 1:1 HCl alone, dissolved only partial amounts of titanium in NBS standard cast irons and steels. However, digestion in 1:1 HCl followed by addition of 30%  $\text{H}_2\text{O}_2$  and a second digestion dissolved total amounts of titanium in those materials.

Oxalic acid solutions of cast iron and steel developed yellow crystalline precipitates within a few weeks after preparation. These precipitates, probably ferrous oxalate, may have formed by photochemical reduction of ferric ion as proposed by Riggs and Bricker (2). However, oxalic acid solutions of cast iron and steel which were gassed with carbon dioxide have remained clear and free of precipitate while standing for 3 years.

In early fusion experiments, melts of 0.1000-gram samples with 4.00 grams of potassium pyrosulfate dissolved readily in 0.3M oxalic acid. On standing overnight, however, colorless crystals formed in the prepared solutions. These crystals 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.

Fusion melts with sodium bisulfate ( $\text{NaHSO}_4$ , fused) formed no corresponding crystals in dilute oxalic acid. However, fusions with sodium bisulfate solubilized only partial amounts of the titanium in NBS standard samples of bauxite, magnetite iron ore, alumina refractory, and burned magnesite. Total amounts of titanium in these materials were obtained, however, by the recommended fusion with sodium carbonate.

**Spectrophotometric Procedure.** Previous tiron procedures (1, 3-6) were encumbered by hydrolytic precipitation of metatitanic acid. To circumvent this disturbing hydrolysis, the above authors conducted the tiron reaction in unfavorably strong mineral acid solutions. In the present method, oxalic acid prevents hydrolysis of titanium, and color development proceeds in clear solutions under optimal pH conditions.

In dilute oxalic acid solutions, 10 mg of iron(II) produced bright yellow ferrous oxalate which crystallized on standing (7, p 318). The yellow oxalate also developed in oxalic acid solutions containing 10 mg of iron(III) after the addition of sodium dithionite. Introduction of 5 ml of 0.1M disodium

**Table I. Effect of pH on Color Development of Titanium-Tiron Complex<sup>a</sup>**

pH	Absorbance at 420 nm	Effect
4.0	...	Turbidity and ppt after $\text{Na}_2\text{S}_2\text{O}_4$
4.5	...	Turbidity for 120 min after $\text{Na}_2\text{S}_2\text{O}_4$
4.8	...	Turbidity for 70 min after $\text{Na}_2\text{S}_2\text{O}_4$
5.0	0.186	
5.1	0.194	
5.2	0.204	
5.3	0.204	
5.4	0.206	
5.5	0.206	
5.6	0.204	Maximum color after standing 30 min
6.0	...	Maximum color not developed in 60 min

<sup>a</sup> Each 50-ml test solution contained 50  $\mu\text{g}$  of standard titanium.

EDTA prior to sodium dithionite completely prevented formation of the yellow ferrous oxalate.

In the present procedure, disodium EDTA did not produce the colored ferric EDTA complex reported by Easton and Greenland (4).

In early buffer trials, 10 ml of 1M sodium acetate (4) was tested in a 50-ml solution containing 100  $\mu\text{g}$  of standard titanium and 10 mg of iron(III). Absorbance of the titanium-tiron complex remained constant less than 2 hours.

Ammonium dihydrogen phosphate was then examined as a combined buffer and stabilizer of ionic iron (8). When solutions of standard titanium and 10 mg of iron(III) were buffered at pH 4.9 to 5.2 with 10 ml of 1M  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{NH}_4\text{OH}$ , the titanium tironate colors remained unchanged at least 1 day. However, solutions buffered with  $\text{NH}_4\text{H}_2\text{PO}_4$  suffered interferences from relatively low amounts of calcium, molybdenum, and tungsten.

Ammonium tartrate showed lower solubility and gave lower titanium tironate absorbances than the other buffers tested.

Ammonium citrate functioned most effectively as buffer and masking agent. Its favorable solubility and buffering capacity facilitated color development of the tiron complex. And its masking action inhibited interference by significant amounts of diverse metallic ions. Ammonium citrate also decreased the absorbance of the reagent blank.

The pH of test solutions affected color development markedly (Table I). At pH 4.0 to 4.8, sodium dithionite produced interfering turbidity; at pH 5.0 and higher, solutions remained clear. Maximum color developed at pH 5.2 to 5.6. Solutions of pH above 5.6 retarded color development. Titanium-tiron complexes maintained longest color stability at pH 5.2 to 5.6.

Reduction with sodium dithionite in the confined space of a 50-ml volumetric flask suppressed full development of titanium tironate color. However, maximum color developed when sodium dithionite was added to the test solution in a 50-ml beaker, stirred thoroughly, and allowed to stand uncovered for 10 min. Probably, titanium(IV) is temporarily reduced by sodium dithionite to titanium(III) which is then reoxidized to color reactive titanium(IV) on exposure to air (7, p 386).

Sodium dithionite, according to earlier investigators (1, 3, 4, 9), produced interfering sulfur turbidity in developed solutions. These authors recommended that absorbances be read within

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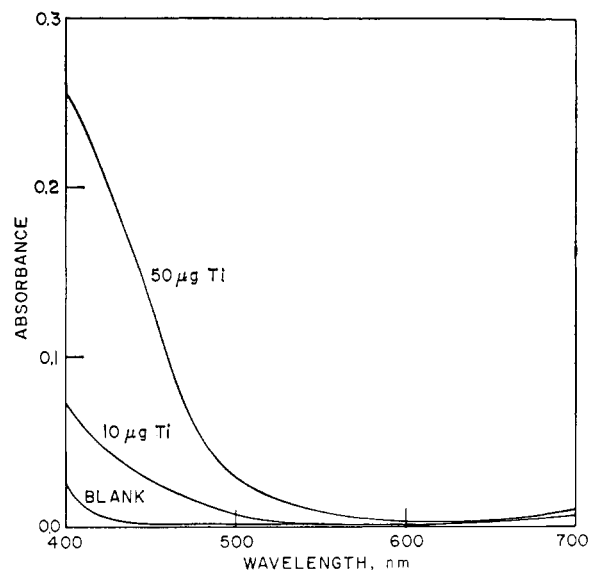
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(6) P. Szarvas and B. Csiszar, *Acta Chim. Acad. Sci. Hung.*, **7**, 403 (1955).

(7) R. K. McAlpine and B. A. Soule, "Qualitative Chemical Analysis," based upon the text by A. B. Prescott and O. C. Johnson, D. Van Nostrand Co., Inc., New York, N. Y., 1933.

(8) L. J. Clark, *ANAL. CHEM.*, **34**, 348 (1962).

(9) L. Shapiro and W. W. Brannock, *U. S. Geol. Survey Bull.*, **1144-A**, 1962, 56 pp.



**Figure 1. Spectral absorbance of titanium-tiron complex in oxalic acid solution**

15 minutes after addition of the reductant. In the present method, sodium dithionite produced no turbidity or precipitate of sulfur.

Thiourea functioned primarily as masking agent for copper. Additionally, it decreased the absorbance of the reagent blank

by approximately one half, thus refining the detectability of the spectrophotometric procedure.

The preceding stabilizing treatments permitted addition of tiron last in sequence under optimal reaction conditions. Maximum color developed within 30 min after addition of the cold tiron solution.

Color intensities were measured at a wavelength of 420 nm, somewhat below peak absorbance at 380 nm (1). At 420 nm, the spectral curves (Figure 1) show a low absorbance for the reagent blank and effectively high absorbances for 10 and 50 µg of standard titanium.

Color stabilities of three 50-ml test solutions containing 0, 10, and 50 µg of standard titanium were determined in stoppered cuvettes at different wavelengths. At 400 and 410 nm, the absorbances of each solution decreased within 1 day. At 420 and 430 nm, the absorbances of these same solutions remained constant for 16 days.

Over the range 0 to 100 µg of titanium in 50 ml, absorbance *vs.* concentration conformed to Beer's law. On the calibration curve, 10 µg of titanium in 50 ml showed an absorbance of 0.041 unit.

**Effect of Diverse Ions.** Metals commonly associated with titanium were selected for interference tests (Table II). Initially, 1000 µg of each metallic ion (corresponding to 10% sample content) was subjected to the recommended spectrophotometric procedure. If the resulting absorbance exceeded that of the reagent blank, decreasing amounts of the ion were

**Table II. Absorbances of Diverse Metallic Ions with Tiron in Oxalic Acid Solution**  
Introduced metallic ion

Ion	Source	Amount		Absorbance at 420 nm	Equivalent as Ti, µg
		In test soln, µg in 50 ml	In sample, % in 0.1 g		
Aluminum(III)	AlCl <sub>3</sub> ·6H <sub>2</sub> O	1000	10.0	0.000	0.0
Calcium(II)	CaCO <sub>3</sub>	1000	10.0	0.000	0.0
Chromium(III)	CrCl <sub>3</sub> ·6H <sub>2</sub> O	250	2.5	0.000	0.0
		300	3.0	0.004	1.0
		400	4.0	0.005	1.2
		1000	10.0	0.014	3.4
		3000 <sup>a</sup>	30.0	0.000	0.0
		10000 <sup>a</sup>	100.0	0.000	0.0
Cobalt(II)	CoCl <sub>2</sub> ·6H <sub>2</sub> O	1000	10.0	0.000	0.0
Copper(II)	CuCl <sub>2</sub> ·2H <sub>2</sub> O	1000	10.0	0.000	0.0
Iron(III)	FeCl <sub>3</sub> ·6H <sub>2</sub> O	10000	100.0	0.000	0.0
Magnesium(II)	MgO	1000	10.0	0.000	0.0
Manganese(II)	MnCl <sub>2</sub> ·4H <sub>2</sub> O	1000	10.0	0.000	0.0
Molybdenum(VI)	MoO <sub>3</sub>	30	0.3	0.000	0.0
		40	0.4	0.004	1.0
		100	1.0	0.009	2.2
		1000	10.0	0.098	23.9
		1000	10.0	0.000	0.0
Nickel(II)	NiO	1000	10.0	0.000	0.0
Niobium(V)	Nb metal	25	0.25	0.000	0.0
		30	0.30	0.002	0.5
		100	1.0	0.016	3.9
		1000	10.0	0.119	29.0
		1000	10.0	0.000	0.0
Silicon(IV)	Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	1000	10.0	0.000	0.0
Tantalum(V)	Ta <sub>2</sub> O <sub>5</sub>	25	0.25	0.000	0.0
		30	0.30	0.002	0.5
		100	1.0	0.008	1.9
		1000	10.0	0.071	17.3
		1000	10.0	0.000	0.0
Tin(II)	SnCl <sub>2</sub> ·2H <sub>2</sub> O	1000	10.0	0.000	0.0
Tungsten(VI)	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	400	4.0	0.000	0.0
		500	5.0	0.003	0.7
		1000	10.0	0.013	3.2
		400	4.0	0.000	0.0
		500	5.0	0.002	0.5
Vanadium(V)	NH <sub>4</sub> VO <sub>3</sub>	1000	10.0	0.005	1.2
Zinc(II)	Zn metal	1000	10.0	0.000	0.0
Zirconium(IV)	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	1000	10.0	0.000	0.0

<sup>a</sup> Chromium at 3000 and 10000 µg was volatilized as chromyl chloride.

Table III. Determination of Titanium in NBS Standard Reference Materials

SRM No.	Material	Sample wt, gram	Titanium, %		Difference
			NBS certificate	By tiron method	
4i	Cast iron	0.1	0.026	0.027	+0.001
7g	Cast iron	0.1	0.044	0.044	0.000
19g	Steel, A.O.H.	0.1	0.027	0.027	0.000
170a	Steel, B.O.H.	0.1	0.281	0.279	-0.002
69a	Bauxite	0.5	1.68 <sup>a</sup>	1.72	+0.04
29a	Magnetite iron ore	0.1	0.09 <sup>a</sup>	0.09	0.00
76	Alumina refractory	0.1	1.32 <sup>a</sup>	1.31	-0.01
104	Burned magnesite	0.5	0.018 <sup>a</sup>	0.020	+0.002
99	Feldspar	0.5	0.010 <sup>a</sup>	0.010	0.000
97	Flint clay	0.5	1.43 <sup>a</sup>	1.45	+0.02
81	Glass sand	0.5	0.057 <sup>a</sup>	0.057	0.000

<sup>a</sup> Ti value was calculated from NBS certificate value for TiO<sub>2</sub>.

tested until the tolerance limit was reached. For each metal, except chromium and iron, 1000 µg of the ion was the highest amount tested.

No interfering absorbance was produced by 1000 µg each of aluminum(III), calcium(II), cobalt(II), copper(II), magnesium(II), manganese(II), nickel(II), silicon(IV), tin(II), zinc(II), or zirconium(IV). No net absorbance was produced by 10,000 µg of iron(III). No absorbance was shown by 250 µg of chromium(III), 400 µg of tungsten(VI), or 400 µg of vanadium(V). Only 30 µg of molybdenum(VI), 25 µg of niobium(V), or 25 µg of tantalum(V) was tolerated without interference.

Calcium, in the absence of ammonium citrate, developed incipient turbidity at the 600-µg level. However, when citrate was present, 1000 µg of calcium produced no turbidity or other interference.

Chromium, in amounts to 250 µg (2.5% of sample), showed no interference. However, 300 µg of chromium in test solutions produced a disturbing absorbance.

Interference by more than 2.5% of chromium was eliminated by volatilization of chromium prior to the determination of titanium. The procedure used for volatilization of chromium as chromyl chloride, based on the study by F. W. Smith (10), was developed and recommended by O. R. Gates (11) as follows:

Transfer the sample aliquot containing 0 to 10 mg of chromium to a 50-ml beaker. Add 5 ml of concd nitric acid and 3 ml of perchloric acid (70%). Cover and heat to boiling on a hot plate in 15 min. Heat briefly to strong fumes above a Fisher burner, and replace on the hot plate. Steadily pipet 0.5 ml of concd hydrochloric acid down the wall of the beaker. Copious fumes of chromyl chloride will be evolved. Again heat to fumes and repeat the treatment with 0.5 ml of HCl. After three volatilizations, rinse with a few ml of water, evaporate to dryness, and dissolve the residue with 1 ml of 1:1 HCl. (For determination of titanium, add 10 ml of 0.3M oxalic acid solution.)

The volatilization of 10 mg of chromium from test solutions containing 10 µg of standard titanium showed no interfering effect on the absorbance of the titanium tironate. When a 0.1000-gram sample is taken, the volatilization treatment permits determination of microgram amounts of titanium in materials containing up to 100% chromium.

Copper(I) or copper(II) interfered seriously in initial experiments. Addition of 10 µg of copper produced an absorbance

of 0.005, and 1000 µg of copper formed a dark turbid precipitate with sodium dithionite. Thiourea, mentioned by Sandell (12, p 199) as a copper complexer, was introduced in liquid and solid forms. Tests showed that 1 gram of granular thiourea, added after sodium dithionite, eliminated all interference by 1000 µg of copper. With thiourea present, 1000 µg of copper showed no effect on the absorbance of 10 µg of standard titanium.

Iron, as ferric chloride, formed an intense purple complex with tiron as described by Yoe and Jones (13). A later study (1) showed that sodium dithionite bleached the colored complex by reduction of ferric ion to the nonreactive ferrous state. However, reduced solutions of the reported (1) samples (which contained less than 2% iron) remained stable only 15 minutes.

In the present method, reduction with sodium dithionite prior to addition of tiron prevented formation of the colored ferric complex. In 50-ml test solutions, 200 mg of sodium dithionite kept 10 mg of iron(III) [sample of 100% iron(III)] reduced and free of ferric tironate at least 1 day and usually longer. When reduced by this modified dithionite treatment, 10 mg of iron(III) showed no interfering effect on the tironate color of 10 µg of standard titanium.

Molybdenum produced a bright yellow compound with tiron as reported by Yoe and Jones (13). In solutions buffered with ammonium phosphate, as little as 10 µg of molybdenum caused color interference. In later tests ammonium citrate eliminated interfering absorbance by 30 µg of molybdenum. More than 0.3% of molybdenum should be separated from the sample before determination of titanium.

Recently, Pyatnitskii and Grigalashvili (14) reported a tiron procedure for the determination of 6 to 100 µg of titanium in the presence of 200 µg of molybdenum and 300 µg of tungsten. The authors used citric acid and the sodium salt of glycolic acid as combined masking and buffering agents. (Glycolic acid, it should be noted, is closely related to oxalic acid in structure and reactions.)

Niobium and tantalum formed similar yellow complexes with tiron at pH 5.2 to 5.6. Only 25 µg of niobium or tantalum could be tolerated without interference, and 30 µg of either element produced incipient interfering absorbances.

Tungsten, in amounts from 10 to 1000 µg, produced no

(10) F. W. Smith, *IND. ENG. CHEM., ANAL. ED.*, **10**, 360 (1938).

(11) O. R. Gates, Naval Research Laboratory, Washington, D. C., personal communication, 1968.

(12) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed., Interscience Publishers, Inc., New York, N. Y., 1959.

(13) J. H. Yoe and A. L. Jones, *IND. ENG. CHEM., ANAL. ED.*, **16**, 111 (1944).

(14) I. V. Pyatnitskii and K. I. Grigalashvili, *Soobshch. Akad. Nauk Gruz. SSR*, **56**, 89 (1969).

visually detectable color with tiron. Spectrophotometric measurements, however, showed slight positive absorbances by 500 and 1000  $\mu\text{g}$  of the metal. Ammonium citrate acted more effectively than ammonium phosphate, ammonium tartrate, or tartaric acid in controlling tungsten interference.

Vanadium at the 400- $\mu\text{g}$  level caused no interfering absorbance. However, 1000  $\mu\text{g}$  of vanadium produced an absorbance equal to that developed by approximately 1  $\mu\text{g}$  of titanium.

Fluoride reportedly (1) interferes in the titanium-tiron reaction. The present method excludes fluoride as a reagent, and thus avoids a contaminating source of interference.

**Stability.** Solutions of samples prepared in dilute oxalic acid have remained clear and free of precipitate for 3 years with apparently indefinite stability.

Test solutions of standard titanium tironates in stoppered cuvettes showed constant absorbances during periods of 2 weeks. Titanium test solutions containing diverse metallic ions remained color stable at least 1 day after development with tiron.

From 2 to 100  $\mu\text{g}$  of titanium can be determined in 50-ml

test solutions. Depending on the aliquot taken, the sensitivity and range permit determination of 0.02 to 10.0% of titanium in 0.1000-gram samples, or 0.004 to 2.00% of titanium in 0.5000-gram samples.

The precision of the spectrophotometric procedure, only, was estimated from the absorbances of a series of test solutions containing 50  $\mu\text{g}$  of titanium. The standard deviation between measurements was calculated to be  $\pm 0.3 \mu\text{g}$  of titanium, equal to a relative deviation of  $\pm 0.6$  percent.

The accuracy of the overall method is shown by comparative results in Table III on eleven Standard Reference Materials certified by the National Bureau of Standards. The titanium determinations by the tiron method agree favorably with the NBS analytical values.

**Applications.** Although developed primarily for high-iron samples, this spectrophotometric method can be used to determine titanium in a wide variety of inorganic materials including metals, alloys, minerals, and rocks.

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## Spectrophotometric Determination of Sulfite with 4,4'-Dithiodipyridine and 5,5'-Dithiobis(2-Nitrobenzoic Acid)

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**Sulfite ion reacts essentially quantitatively at room temperature in aqueous buffers with 4,4'-dithiodipyridine and 5,5'-dithiobis(2-nitrobenzoic acid) to displace the thiol and form an organic thiosulfate. Sulfite is determined by measurement of the absorption of the thiol. The reaction is useful for the determination of sulfite over a concentration range of approximately 0.2 to 6.0  $\mu\text{g}/\text{ml}$  as  $\text{SO}_3$ . The pH value is not critical and can be varied over a range of 3-4 units. The disulfide and reaction solutions are reasonably stable. Some possible metal ion interferences, except for  $\text{Hg}(\text{II})$ , can be eliminated by use of EDTA. Other thiols, thiosulfate, sulfide, and cyanide ion will interfere. Nitrite ion does not appear to cause any difficulty. Sulfite solutions were quite stable when EDTA was present.**

SULFITE ION reacts with many organic disulfides to displace a thiol anion and form the organic thiosulfate, commonly called a "Bunte" salt. This reaction proceeds as shown in Equation 1.



This reaction was recently reviewed by Klayman and Shine (1). In almost all instances, a large excess of sulfite ion is used in order to have quantitative reaction of the disulfide. The thiol anion is then titrated with silver nitrate (2) or

mercuric chloride (3). Some nitro-substituted aromatic disulfides have been reported to react readily with sulfite ion, using a rather small excess of sulfite (4) or having equimolar amounts of sulfite and disulfide (5, 6). Room temperatures are generally used for the sulfite-disulfide reactions although in one study (4), several substituted aromatic disulfides were refluxed with excess sulfite in aqueous methanol. There appear to be no detailed studies of the reaction of aromatic disulfides with sulfite ion in the literature.

Certain disulfides, notably 5,5'-dithiobis(2-nitrobenzoic acid), "Ellman's" reagent (7), DTNB, and 4,4'-dithiodipyridine (8), 4-PDS, are used frequently for the determination of thiol groups in a variety of biochemical samples. The disulfide is reduced to the corresponding thiol which absorbs at a different wavelength than the disulfide. Since the disulfide is present in excess when thiol groups are determined by this method, presumably a mixed disulfide is formed and the absorbing thiol displaced as shown in Equation 2.



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