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Determination of Titanium in Some Metallurgical Materials by Atomic Absorption Spectrophotometry

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The atomic absorption spectrophotometric determination of titanium was subject to interference by other elements in a nitrous oxide-acetylene flame with a Perkin-Elmer Model 303 atomic absorption spectrophotometer, fitted with a 5-cm long-path slot burner. The effects of various other elements, acids, and water-miscible organic solvents on the titanium atomic absorption were examined. Aluminum produced the greatest enhancement of the titanium absorption of all the elements examined. Both butyric acid (2.0 M) and diethylene glycol monobutyl ether (20%) enhanced the titanium absorption by about 100% in aqueous solutions. In the presence of 5000 ppm aluminum or 20% diethylene glycol monobutyl ether, the interferences from other elements appeared to be completely removed. Furthermore, the extraction of titanium with cupferron into methyl isobutyl ketone was successful in effecting an increase in the sensitivity of titanium and in eliminating, or at least diminishing the interferences from other elements. The atomic absorption method was then applied to the determination of titanium in ferric oxides, nickel-chromium steel, nickel alloy, and steels with satisfactory results.

Titanium is one of the elements which are difficult to determine by means of atomic absorption spectrophotometry because it forms a stable refractory oxide in the flame. However, after Amos and Willis[1] introduced a nitrous oxide-acetylene flame into atomic absorption spectrophotometry, many refractory elements including titanium have become determinable by means of atomic absorption spectrophotometry. Headridge and Hubbard[2] reported the atomic absorption spectrophotometric determination of titanium in steels, permanent magnet alloys, and cast iron with hydrofluoric acid solutions. Bowman and Willis[3] obtained satisfactory results in the determi-

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[1] M. D. Amos and J. B. Willis, *Spectrochim. Acta*, **22**, 1325 (1966).

[2] J. B. Headridge and D. P. Hubbard, *Anal. Chim. Acta*, **37**, 151 (1967).

[3] J. A. Bowman and J. B. Willis, *Anal. Chem.*, **39**, 1210 (1967).

nation of titanium in bauxite and steel. Amos and Willis[1] found that iron at the 2000 ppm level in the presence of 20% hydrofluoric acid considerably enhanced the titanium atomic absorption. Recently Kirkbright *et al.*[4] reported the sensitive, indirect determination of titanium by means of atomic absorption spectrophotometry, with the extraction of molybdotitanophosphoric acid into butyl alcohol.

The effect of organic solvents has been well studied on the atomic absorption of many elements, but scarecely not at all on the atomic absorption of titanium. In this investigation, the effects of various extraneous elements and water-miscible and immiscible organic solvents on titanium absorption in a nitrous oxide-acetylene flame were investigated. Many elements interfered with the titanium absorption, but effective means, including solvent extraction, were found to eliminate the interferences. This paper will also describe the results of the atomic absorption spectrophotometric determination of titanium in ferric oxides, steels, and a nickel-base alloy.

Experimental

Table 1. Operating conditions for titanium absorption

Wavelength	364.3 nm
Slit-width	0.3 mm
Spectral bandpass	0.2 nm
Lamp current	40 mA
Scale expansion	×1
Nitrous oxide flow rate under the pressure of 30 p.s.i.	14.0 l/min
Acetylene flow rate under the pressure of 8 p.s.i.	7.6 l/min for aqueous solution
	6.4 l/min for methyl isobutyl ketone
Flame height	3 mm above burner head
Burner slot	0.48 mm×50 mm

Apparatus. A Perkin-Elmer Model 303 atomic absorption spectrophotometer, equipped with a nitrous oxide burner head, was used in this work. The experimental conditions are shown in Table 1. The titanium 364.3 nm line was slightly less intensive, but it was more strongly absorbed by titanium atoms, than the 365.4 nm line; therefore, the 364.3 nm line was chosen as the analytical absorption line. A Perkin-Elmer titanium hollow-cathode lamp was used as the radiation source. Under the optimum flame conditions, shown in Table 1, about a 3 cm long "red feather" was produced above the burner head, and the sample aspiration rate was about 8.6 ml/min.

Reagents. A stock solution of titanium(5000 ppm) was prepared by dissolving 5.000 g of high-purity titanium sponge (99.99%) with 50 ml of 6 N hydrochloric acid by heating on a hot plate and by then diluting to 1000 ml with distilled water. Various standard titanium solutions were prepared by suitably diluting the stock solution.

A cupferron solution (5%) was prepared by dissolving 5.0 g of cupferron with distilled water. The solution was prepared daily.

All the other chemicals used were of an analytical-reagent grade.

Results and Discussion

Effects of Inorganic Acids. The effects of the inorganic acids generally used for sample decomposition were studied in the concentration range of 0—2.0 N on a 100 ppm titanium solution. The acids studied were hydrochloric, hydrofluoric, nitric, perchloric, phosphoric, and sulfuric acids. Hydrochloric and nitric acids had no effect on the titanium absorption, even at higher concentrations up to 6.0 N. The other acids enhanced the titanium atomic absorption, as is shown in Fig. 1.

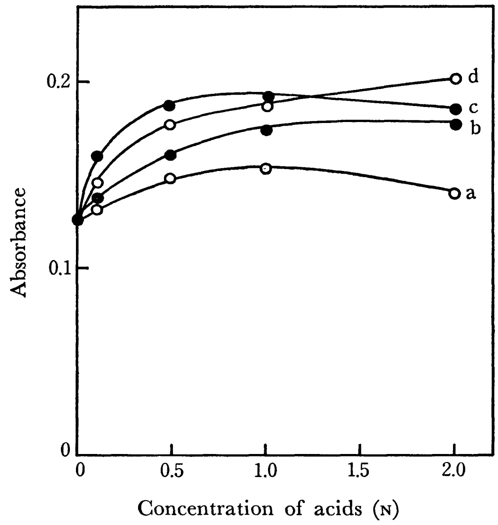

Fig. 1. Effect of inorganic acids on titanium atomic absorption.
Concentration of titanium: 100 ppm.
(a) Sulfuric acid; (b) phosphoric acid; (c) perchloric acid; (d) hydrofluoric acid.

As has been described by Amos and Willis,[1] the enhancement by hydrofluoric acid is possibly due to the inhibition of the formation of titanium monoxide in the flame by forming a more stable fluoro-complex, which decomposes easily at the temperature of the nitrous oxide-acetylene flame. Since sulfate and phosphate ions are known to form complexes with titanium, the enhancement by sulfuric and phosphoric acids may be explained, as in the case of hydrofluoric acid, in terms of the inhibition of monoxide formation, but the enhancement by perchloric acid, the extent of which is nearly equal to that by hydrofluoric acid, is difficult to explain because of its inability to form stable complexes with titanium. At any rate, when hydrofluoric acid and/or perchloric acid are used in the sample decomposition, the acid concentrations of the sample solution and the standard solution should match.

Effects of Organic Acids. The effects of monocarboxylic acids, *i.e.*, formic, acetic, trichloroacetic, propionic, and butyric acids, on the titanium absorption were also studied. The absorption measure-

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4) G. F. Kirkbright, A. M. Smith, and T. S. West, *Analyst*, **94**, 754 (1969).

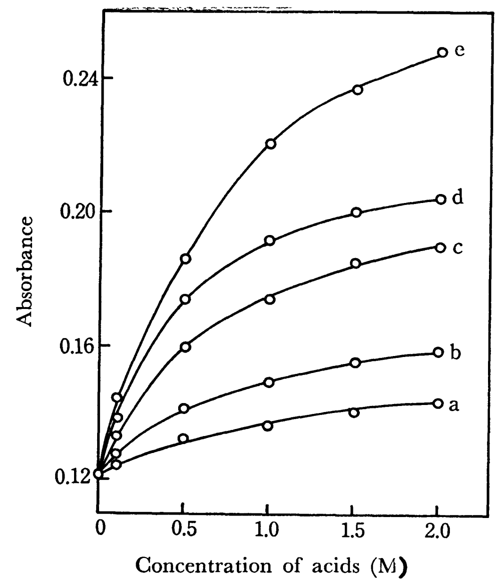

Fig. 2. Effect of organic acids on titanium atomic absorption.
Concentration of titanium: 100 ppm.
(a) Formic acid; (b) acetic acid; (c) propionic acid; (d) trichloroacetic acid; (e) butyric acid.

TABLE 2. EFFECT OF OTHER ELEMENTS ON TITANIUM ABSORPTION

Element	Recovery of Ti (%) Aqueous solution	Recovery of Ti (%) Solvent extraction	Element	Recovery of Ti (%) Aqueous solution	Recovery of Ti (%) Solvent extraction
None	100	100	Mn[d,f]	115	99
Al[a,f]	170	101	Mo[e,f]	141	62
As[b]	125	101	Na[a]	98	99
Au[a]	111	102	Ni[c,f]	104	99
Ba[a]	111	100	Pb[d]	105	102
Be[c]	140	98	Pd[a]	116	100
Bi[d,f]	107	99	Rb[a]	102	100
Ca[d,f]	135	99	Sb[a,f]	42	102
Cd[d,f]	109	100	Se[b]	25	101
Ce[c,f]	146	102	Si[b,f]	146	98
Co[d,f]	115	98	Sn[a,f]	117	103
Cr[d]	121	99	Sr[d]	105	99
Cs[a]	114	101	Te[b]	119	100
Cu[d,f]	116	102	Th[d,f]	127	95
Fe[a,f]	118	62	Tl[a]	109	99
Hg[a,f]	110	96	V[e,f]	121	55
In[a,f]	113	99	W[b,f]	105	95
K[a]	112	101	Y[b,f]	148	98
La[a,f]	148	99	Zn[a,f]	112	102
Li[a]	112	101	Zr[d,f]	130	35
Mg[d,f]	128	97			

Concentration of the elements added, 1000 ppm; titanium added, 100 ppm.

a) Added as chloride. b) Added as sodium arsenite, selenite, silicate, tellurite or tungstate, respectively. c) Added as sulfate. d) Added as nitrate. e) Added as ammonium molybdate or vanadate, respectively. f) Element chelating with cupferron.

ments were made on a 100 ppm titanium solution in the presence of the acids, the concentrations of which were changed from 0.1 to 2.0 M. These acids produced an enhancement, and the titanium absorptions were increased, with an increase in the acid concentrations, as is shown in Fig. 2. Butyric acid was the most effective, enhancing the titanium absorption 2-fold at 2.0 M. The enhancing effect of these acids is probably due to the formation of stable complexes of titanium, which decompose easily in the flame. On the other hand, these acids may play the same role as organic solvents, as will be discussed later, since the enhancement in the presence of the acids increased with an increase in the carbon numbers, the molecular weight, and the boiling point except in the case of trichloroacetic acid.

Effects of Various Other Elements. Amos and Willis[1] have reported the enhancing effects of hydrofluoric acid and of iron in the determination of titanium. Headridge and Hubbard[2] have described that there is no interference from various foreign elements, such as chromium, cobalt, manganese, molybdenum, nickel, niobium, sulfur, tantalum, tungsten, and vanadium, in the presence of iron in the aqueous ethanolic hydrofluoric acid solution, and that aluminum interferes with the determination of titanium.

The effects of various other elements on the atomic absorption of titanium were studied at constant concentration levels in aqueous solutions. The elements examined and their effects on the atomic absorption of titanium are shown in Table 2. The concentration of titanium was 100 ppm, and that of the interferent, 1000 ppm. Table 2 indicates that most elements except for antimony and selenium enhanced the titanium absorption. It is also evident from Table 2 that such elements as aluminum, beryllium, cerium, lanthanum, and silicon, which are apt to form stable oxides in the flame, produced a greater enhancement. Aluminum produced the greatest enhancement. Such an enhancement is possibly caused by competition between titanium and the other refractory elements to form stable oxides in the flame, as has been described in the case of aluminum[5] and vanadium[6] by Robinson *et al.*, but the enhancement cannot be explained completely satisfactorily. The decreasing effect of antimony and selenium is ascribable to the formation of insoluble precipitates in aqueous solutions. Although bismuth and thallium produced insoluble precipitates, they slightly enhanced the titanium absorption.

Thus, titanium absorption suffers serious interference from many elements, so a suitable means for eliminating or suppressing them must be found. Otherwise, atomic absorption will be of little analytical use. David[7] has already demonstrated that aluminum suppresses interferences from other elements in the determination of molybdenum in an air-acetylene flame. In this study, the suppressing effect of aluminum on the interferences with titanium absorption was studied. At first, the effect of an increase in the

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5) T. V. Ramakrishna, P. W. West, and J. W. Robinson, *Anal. Chim. Acta*, **39**, 81 (1967).

6) S. L. Sachdev, J. W. Robinson, and P. W. West, *ibid.*, **37**, 12 (1967).

7) D. J. David, *Analyst* (London), **86**, 730 (1961).

concentration of aluminum was studied on 100 ppm of titanium; it was found that the titanium absorption was increased with an increase in the aluminum concentration until a constant enhancement was attained at more than 2000 ppm of aluminum. Then, in the presence of aluminum at 5000 ppm the effects of various other elements were studied at the 1000-ppm concentration level. None of the elements listed in Table 2 showed any more effect on the titanium absorption; thus, the interferences from other elements on titanium absorption appeared to disappear completely. Furthermore, the titanium absorption was measured in the presence of aluminum (5000 ppm) by varying the concentrations of the interferents. Figure 3 shows the results, with iron as an example. Similar results were obtained with other interferents.

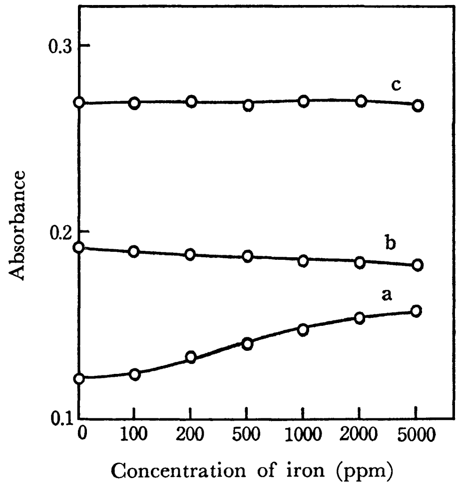

Fig. 3. Suppressing effect of aluminum and diethylene glycol monobutyl ether on the interference from iron with titanium atomic absorption.
Concentration of titanium: 100 ppm.
(a) With no addition; (b) with the addition of aluminum (5000 ppm); (c) with the addition of diethylene glycol monobutyl ether (20 vol%)

Effects of Water-miscible Organic Solvents. Atomic absorptions were measured on 100 ppm titanium solutions containing water-miscible organic solvents, such as alcohols, ketones, and glycols, at 10 vol%. The results are shown in Table 3. Among the alcohols, butyl alcohol produced the greatest enhancement, and very stable chart readings were obtained in its presence. Glycols produced greater enhancements. The greatest enhancement was produced by diethylene glycol monobutyl ether, which had previously reported to be very effective in the enhancement of vanadium absorption in a nitrous oxide-acetylene flame.[6] The effect of an increase in the concentration of diethylene glycol monobutyl ether on the titanium absorption was studied; it was found that about 20 vol% of diethylene glycol monobutyl ether increased the absorption by about 100% and that concentrations higher than 20 vol% did not produce further enhancement.

It can be seen from Table 3 that the organic solvents with higher boiling points and longer carbon chains increased the titanium absorption more, and that the absorption was contrary to the increase in the sample aspiration rate when the enhancement effect was compared in its extent among solvents of the same kinds.

Interferences from other elements with titanium

TABLE 3. EFFECT OF WATER-MISCIBLE ORGANIC SOLVENTS ON TITANIUM ABSORPTION

Solvent	Molecular weight	Boiling point (°C)	Sample aspiration rate (ml/min)	Absorbance	Enhancement
None	—	—	8.6	0.125	1.00
Methanol	32.0	64.1	7.9	0.142	1.14
Ethanol	46.1	78.3	7.6	0.136	1.09
Isopropyl alcohol	60.1	82.4	7.2	0.145	1.16
Propyl alcohol	60.1	97.4	7.1	0.158	1.26
Isobutyl alcohol	74.1	107.9	6.6	0.176	1.41
Butyl alcohol	74.1	117.7	6.9	0.189	1.51
Acetone	58.0	56.5	8.1	0.133	1.06
1,4-Dioxane	88.1	101.1	6.0	0.143	1.14
Methyl ethyl ketone	72.1	79.6	8.2	0.177	1.42
Ethylene glycol	62.1	197.7	8.3	0.171	1.37
Ethylene glycol monomethyl ether	76.1	124.5	7.9	0.179	1.43
Ethylene glycol dimethyl ether	90.1	84.7	7.7	0.180	1.44
Ethylene glycol monoethyl ether	90.1	134.8	7.9	0.186	1.49
Diethylene glycol monoethyl ether	134.2	195	7.7	0.200	1.60
Diethylene glycol diethyl ether	162.2	186	7.2	0.224	1.79
Diethylene glycol monobutyl ether	162.2	230	7.2	0.253	2.02

Concentration of the solvents added, 10 vol%; titanium added, 100 ppm.

absorption were studied in the presence of 20 vol% of diethylene glycol monobutyl ether. As in the case of a large amount of aluminum, the interferences seemed to disappear completely. Some representative results are shown in Fig. 3. This fact suggests that diethylene glycol monobutyl ether competes with other elements, as aluminum does, in suppressing the formation of titanium monoxide by providing the flame with reducing properties through the burnt gases. The difference in titanium absorbance observed between Curves b and c in Fig. 3 is probably due to the difference in the efficiencies of the nebulizing sample solutions. It seems, therefore, that diethylene glycol monobutyl ether, a representative water-miscible organic solvent, plays a dual role, *i.e.*, as an atomizing aid and a nebulizing aid, in enhancing the titanium atomic absorption.

Extraction of Titanium Complexes into Organic Solvents. Extractions were carried out with the following reagents for titanium: cupferron,[8] 8-hydroxyquinoline,[9] *N*-benzoyl-*N*-phenyl hydroxylamine,[10] morin,[11] and quinalizarin.[12] Of these, the first three proved to be applicable to the atomic absorption spectrophotometric determination of titanium. The chelates of titanium with morin and quinalizarin were not extracted into methyl isobutyl ketone, which is well known to be suitable for atomic absorption measurements. Cupferron was finally selected as the best chelating reagent. The extraction procedure for titanium cupferrate was as follows: standard solutions containing 10, 20, 30, 40, and 50 μg/ml of titanium were prepared by diluting a stock solution of titanium. A 10-ml aliquot of each standard solution was then placed in a 100-ml separatory funnel, and 40 ml of 1.2 N hydrochloric acid was added. Then 2 ml of a 5% cupferron solution was added, and the titanium cupferrate formed in the solution was extracted into 10 ml of methyl isobutyl ketone with shaking for two minutes. The organic phase which was thus separated, after dehydration with anhydrous sodium sulfate, was sprayed into the flame. The titanium absorption was measured in the nitrous oxide-acetylene flame under the optimum operating conditions described in Table 1. As is shown in Fig. 4, the most sensitive results were obtained with cupferron.

Furthermore, the extractions of titanium cupferrate were carried out with mixed organic solvents of methyl isobutyl ketone containing 25% of oleic acid, as had been done by Sachdev *et al.*[13] in the case of vanadium using an oxygen-acetylene flame created by a total-consumption nebulizer-burner. However, the effects of mixed organic solvents were not as compared with that of methyl isobutyl ketone alone by aspirating the organic extract into the nitrous oxide-acetylene flame.

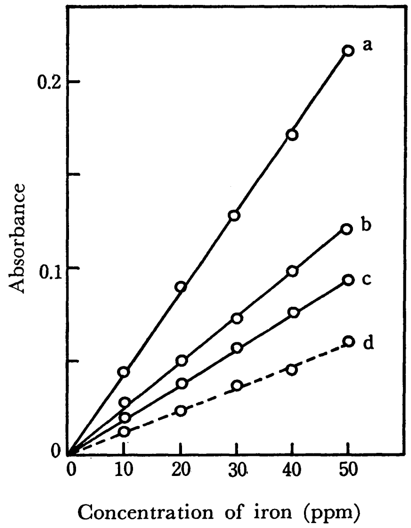

Fig. 4. Calibration graphs for titanium.
(a) Titanium cupferrate; (b) titanium *N*-benzoyl-*N*-phenyl hydroxylamine complex; (c) titanium oxinate; (d) titanium aqueous solutions.

Effects of Other Elements: Some elements were extracted along with titanium under the conditions described above. Their effects on titanium absorption were studied by the following procedure: a 5-ml portion of a standard solution containing 100 μg/ml of titanium and 5 ml of other metal solutions (1000 μg/ml) was diluted to 50 ml with 1.2 N hydrochloric acid. The solution was then transferred into a 100-ml separatory funnel and extracted into 10 ml of methyl isobutyl ketone after adding 2 ml of a 5% cupferron solution. The absorption measured on the organic extract was compared with that measured on an organic phase containing the titanium chelate alone. The results are shown in Table 2. With the exception of the elements which can be extracted with cupferron, essentially no interference was observed from the other

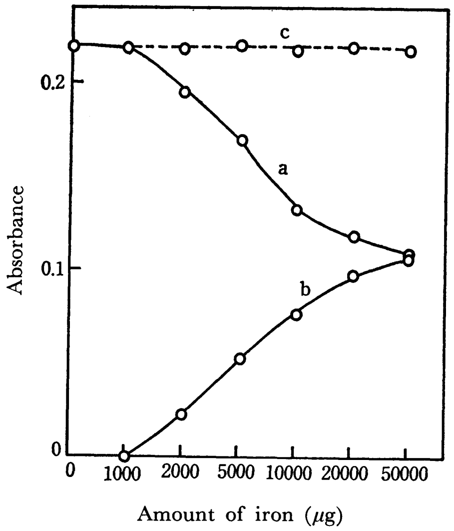

Fig. 5. Solvent extraction of titanium cupferrate in the presence of a large amount of iron.
Amount of titanium: 500 μg (in 10 ml of methyl isobutyl ketone.
(a) Absorbance for the first extraction; (b) absorbance for the second extraction; (c) total absorbance of the first and second extractions.

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[8] N. H. Furman, W. B. Mason, and J. S. Pekola, *Anal. Chem.*, **21**, 1325 (1949).

[9] K. Gardner, *Analyst* (London), **76**, 485 (1951).

[10] S. C. Chome, *ibid.*, **75**, 27 (1950).

[11] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd edn., Interscience Pub., New York (1950), p. 127.

[12] G. Beck, *Mikrochim. Acta*, **34**, 282 (1949).

[13] S. L. Sachdev, J. W. Robinson, and P. W. West, *Anal. Chim. Acta*, **37**, 156 (1967).

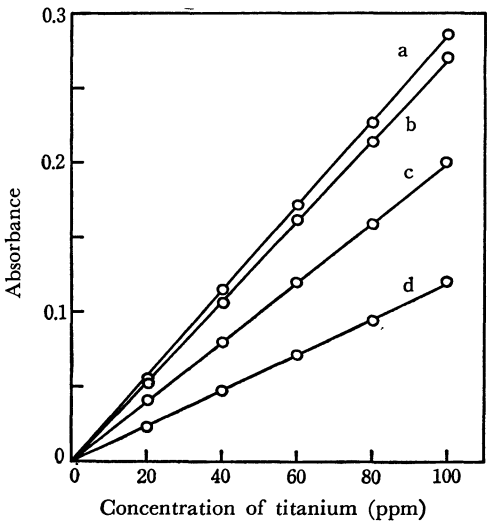

Fig. 6. Calibration graphs for titanium.
(a) In the presence of diethylene glycol monobutyl ether (20 vol%); (b) in the presence of butyric acid (2.0 M); (c) in the presence of aluminum (1000 ppm); (d) titanium alone.

elements present at a concentration 10 times that of titanium. Iron, molybdenum, vanadium, and zirconium, which can be extracted with cupferron, showed depressing effects on the titanium absorption, but the depressing interference could be completely eliminated by successive extractions with two 10-ml portions of methyl isobutyl ketone even if the interfering element was present at a concentration 100 times that of titanium in an aqueous solution, as is shown in Fig. 5. When the concentration of interfering elements was more than 100 times that of titanium, the extraction had to be repeated three times or more. However, a large amount of these interfering elements should preferably be separated before the titanium-cupferrate extraction. Iron, for example, can be extracted as the chloro-complex from 6 N hydrochloric acid solution with methyl isobutyl ketone.

Calibration Graphs for Titanium. Calibration graphs for aqueous titanium, aqueous titanium in the presence of aluminum, butyric acid, and diethylene glycol monobutyl ether, and titanium complexes extracted into methyl isobutyl ketone are shown in Figs. 4 and 6, respectively. Sensitivities for aqueous titanium alone, for aqueous titanium in the presence of aluminum, for aqueous titanium in the presence of butyric acid, for aqueous titanium in the presence of diethylene glycol monobutyl ether, and for titanium complexes with cupferron, *N*-benzoyl-*N*-phenyl hydroxylamine, and 8-hydroxyquinoline extracted into methyl isobutyl ketone were 3.2, 2.0, 1.5, 1.4, 0.8, 1.4, and 1.8 ppm for a 1% absorption respectively.

Application to the Determination of Titanium in Ferric Oxides, Steels, and a Nickel-base Alloy. The present method was then applied to the determination of titanium in ferric oxides, steels, and a nickel-base alloy. The sample was decomposed with the smallest necessary amount of hydrochloric acid and/or nitric acid. After the addition of the amount of aluminum, butyric acid, or diethylene glycol monobutyl ether necessary to bring the final concentration to 5000 ppm, 2.0 M, or 20% respectively, the solution was diluted with distilled water. The resultant solution was sprayed into the nitrous oxide-acetylene flame, and the absorption was measured. The results are shown in Table 4. The results with the methyl-isobutyl-ketone extraction of titanium cupferrate are also shown in Table 4. In this case, iron was separated from the 6 N hydrochloric acid solution with methyl isobutyl ketone before the titanium extraction. The determination was made by referring to the corresponding calibration graphs, shown in Figures 4 and 6. As a result, it was found that the atomic absorption spectrophotometric method could be applied to the determination of titanium in ferric oxides, steels, and a nickel-base alloy with satisfactory results.

TABLE 4. RESULTS OF THE DETERMINATION OF TITANIUM IN A FEW KINDS OF MATERIALS

Sample	Titanium content (%)				
	Cert. value	Atomic absorption method			
		A	B	C	D
Ferric oxide					
No. 1	2.47	2.5_0	2.4_0	2.4_5	2.4_0
No. 2	0.20	0.19	0.19	0.21	0.18
NBS 348 Ni-Cr steel	2.24	2.2_5	2.2_1	2.2_7	2.1_9
BCS No. 310 Ni alloy	2.46	2.4_8	2.4_5	2.4_4	2.4_0
Steel					
No. 100—1	0.12	0.12	0.11	0.12	0.10
No. 102—1	0.24	0.23	0.25	0.24	0.21

A) Determined in the presence of 5000 ppm aluminum.
B) Determined in the presence of 2.0 M butyric acid.
C) Determined in the presence of 20 vol% diethylene glycol monobutyl ether.
D) Determined by the extraction of titanium cupferrate into methyl isobutyl ketone after separation of iron.