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Atomic Absorption Spectrophotometry of Titanium in the Iron Sulfides of NiAs Type

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Synopsis. A method is described for the atomic absorption spectrophotometric determination of titanium in the sulfides, $Fe_{1-x}Ti_xS$ ($x \leq 0.3$), of NiAs type. Potassium sulfate was added to both sample and standard solutions to suppress the iron interference. The powder and single crystal samples were successfully analyzed using 10 mg of samples.

The atomic absorption spectrophotometry of titanium is carried out on iron ores,[1)] cast iron,[2)] ferric oxides,[3)] steels,[2,3)] and alloys[2-4)] using a high temperature flame of nitrous oxide–acetylene. However, titanium forms refractory oxides in the flame and various interference effects are encountered.[3-5)] Therefore, some workers described the necessity of several additives such as aluminium,[1,3)] potassium chloride,[4)] and organic compounds[3)] to suppress the interference of foreign elements in each sample. Iron is known to be one of the interfering elements in the atomic absorption spectrophotometric analysis of titanium.[3-5)] In the present work on the analyses of titanium in the iron sulfides, $Fe_{1-x}Ti_xS$ ($x \leq 0.3$), of NiAs type, the usefulness of the following reagents was examined to suppress the iron interference; hydroxylamine hydrochloride, ammonium fluoride, diammonium salt of EDTA, sodium chloride, potassium chloride, sodium sulfate, and potassium sulfate. Among these reagents, sodium or potassium sulfate was the most effective in suppressing the iron interference. Finally the results of the determination of titanium in the actual samples by a method using potassium sulfate are presented. Ten mg of samples were used for the analysis.

Experimental

Reagents. The standard solution (1 mg Ti/ml) was prepared by dissolving sponge metal (99.5% up) in hydrochloric acid. The solution was stocked as 1 M hydrochloric acid solution. The reagents to be examined as a suppressor for the iron interference were dissolved in deionized water. Reagents used were of analytical reagent grade.

Measurements of Titanium Absorption. The titanium absorption was measured in a nitrous oxide–acetylene flame using a Hitachi model 208 Atomic Absorption Spectrophotometer and a hollow cathode lamp HLA-3. Working conditions used are listed in Table 1. Figure 1 shows effects of the reagents described above on the titanium absorption, where the solutions, except for diammonium salt of EDTA, are adjusted to 0.5 M hydrochloric acid. EDTA solutions are adjusted to pH 4 by adding a minimum amount of ammon-

TABLE 1. WORKING CONDITIONS

Wavelength	364.3 nm
Lamp current	15 mA
Slit setting	Entrance 1 (0.18 mm), Exit 1 (0.18 mm)
Burner height	Scale position 2 (beam height above burner, approximately 20 mm)
Nitrous oxide	1.8 kg/cm^2, 8.0 l/min
Acetylene	0.8 kg/cm^2, 6.0 l/min

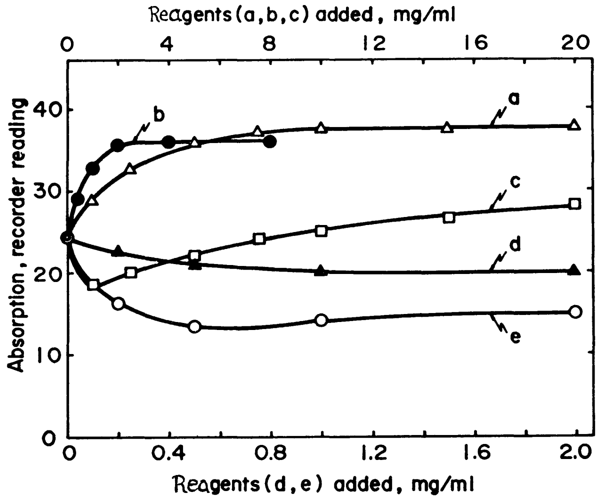

Fig. 1. Effects of several reagents on titanium absorption.
a: $NH_2OH \cdot HCl$, b: NH_4F, c: $EDTA \cdot 2NH_4$, d: NaCl or KCl, e: Na_2SO_4 or K_2SO_4. Ti: 100 ppm.

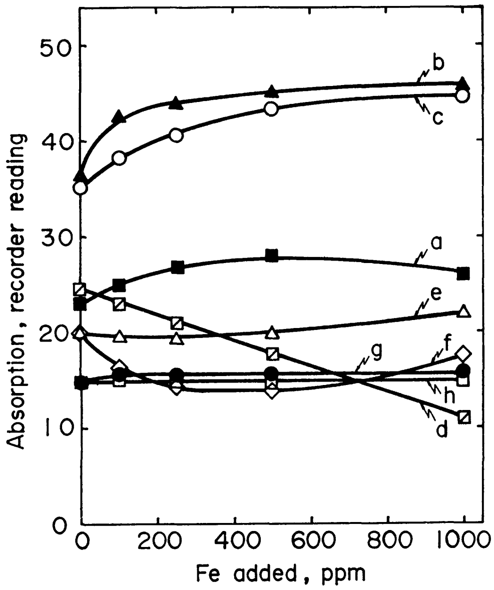

Fig. 2. Effects of iron on titanium absorption in several matrixes.
a: Without other reagents, b: $NH_2OH \cdot HCl$ 20 mg/ml, c: NH_4F 4 mg/ml, d: $EDTA \cdot 2NH_4$ 10 mg/ml, e: NaCl 2 mg/ml, f: KCl 2 mg/ml, g: Na_2SO_4 2 mg/ml, h: K_2SO_4 2 mg/ml. Ti: 100 ppm.

Table 2. Results of analyses

Sample (Nominal composition)	Analyte, wt%						Recovery[a] (%)
	Fe		Ti		S		
	calcd	obsd	calcd	obsd	calcd	obsd	
Powder 1 ($Fe_{0.90}Ti_{0.10}S$)	57.70	58.0	5.50	5.0	36.80	36.5	99.5
Powder 2 ($Fe_{0.80}Ti_{0.20}S$)	51.76	51.8	11.10	11.3	37.14	37.3	100.4
Powder 3 ($Fe_{0.75}Ti_{0.25}S$)	48.75	47.8	13.94	14.1	37.31	37.5	99.4
Crystal 1		58.8		0.2		40.2	99.2
Crystal 2		54.5		4.6		40.4	99.5
Crystal 3		46.8		11.6		41.6	100.0

a) Sum of the observed values for three components.

nium acetate. Reagents which increase the titanium absorption were hydroxylamine hydrochloride and ammonium fluoride. Alkali metal salts such as sodium chloride, potassium chloride, sodium sulfate, and potassium sulfate reduced the titanium absorption. However, at the higher concentration of these reagents the titanium absorption remained constant. At the lower concentration of EDTA the titanium absorption was decreased but the absorption was gradually increased with an increase of the concentration of this reagent.

To suppress the iron interference the effects of these reagents were examined by adding the reagents to the titanium solution containing iron. The concentrations of the reagents added were chosen by the value at which the titanium absorption remained constant (*cf.* Fig. 1). Ferric ions were added as chlorides. The results are shown in Fig. 2. The titanium absorption was increased in the presence of ferric ions in the solution without other reagents. The absorption was higher in hydroxylamine hydrochloride or ammonium fluoride solutions than in the other solutions examined. Though the two reagents highly enhanced the titanium absorption in the presence of ferric ions, they did not suppress the iron interference. EDTA decreased the titanium absorption linearly with an increase of ferric ion concentration. Alkali metal salts reduced the titanium absorption. However, sodium and potassium sulfates gave a constant titanium absorption over a wide range of iron concentrations. In this work, potassium sulfate was used as the suppressor for iron interference.

Analysis of Samples. The powder samples were synthesized by sintering a mixture of the respective elements with the nominal compositions shown in Table 2 at a high temperature, and the crystal structure was identified by X-ray diffraction. The single crystal samples (unknown compositions) were grown by chemical vapor transport. Ten mg of the powder or single crystal samples were dissolved in *aqua regia* containing bromine. After removal of the excess nitric acid by evaporation with hydrochloric acid, the final solution was made up to 25 ml, where the acidity was adjusted to 0.5 M hydrochloric acid and the concentration of potassium sulfate, 2000 ppm. The same adjustment was carried out for standards containing 10 to 100 ppm titanium and the atomic absorption was then measured. The results of the analyses are shown in Table 2, together with the contents of iron and sulfur obtained in separate experiments.[6] For the powder samples, the observed values are in agreement with the calculated values. All the observed values are satisfactory, as the sum of the observed values for three components is close to 100% in all cases.

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