

THE DETERMINATION OF TITANIUM IN TITANIFEROUS MAGNETITE ORES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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INTRODUCTION

Amos and Willis (1) first investigated the use of nitrous oxide for the determination of titanium. They found that the presence of HF and iron enhance the absorption of titanium. They recommended "much more extensive investigation before a practicing chemical analyst can determine this element in a routine fashion by atomic absorption." Various authors (2, 3, 4, 5, 6) have investigated titanium by atomic absorption and have recommended a number of different procedures to remove interference.

In attempting to analyze lithium metaborate fusions (7, 8) of titaniferous magnetite ores of Alaska by atomic absorption, it was found that the interferences are not completely removed by any single approach suggested in the literature. Silicon, iron and aluminum could vary widely between samples and an approach was needed that would

completely eliminate interference effects of all these elements, without having to match the gross matrix composition of samples and standards.

EXPERIMENTAL

The effects of various reagents that would suppress the interferences and a combination of these were first investigated. The effects of  $\text{LiBO}_2$ ,  $\text{NH}_4\text{F}$  and  $\text{SiO}_2$  are shown in Figure 1. In studying the effects of other reagents, the  $\text{LiBO}_2$  concentration is kept constant at 2%, since that is the concentration that results when fusions are dissolved as per the recommended analytical procedure.

For maximum sensitivity, it is necessary to have 2%  $\text{LiBO}_2$ , 0.8%  $\text{NH}_4\text{F}$ , and 0.05 to 0.2%  $\text{SiO}_2$ , corresponding to 12.5 to 50%  $\text{SiO}_2$  in samples when processed as per the recommended analytical procedure. Addition of  $\text{SiO}_2$ ,  $\text{LiBO}_2$  and  $\text{NH}_4\text{F}$  to standards will compensate for interference caused by enhancement of signal due to the presence of  $\text{SiO}_2$  in samples.

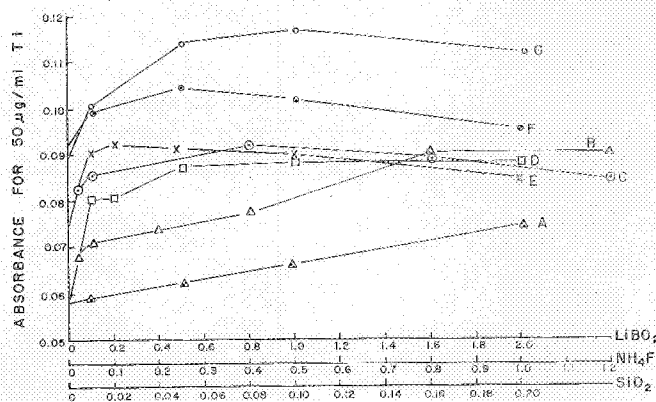


Fig. 1. Effect of various interference suppressing agents on the absorbance of 50 µg/ml Ti solution

- A. Variable  $\text{LiBO}_2$
- B. Variable  $\text{NH}_4\text{F}$
- C. Variable  $\text{NH}_4\text{F}$ ; constant 2%  $\text{LiBO}_2$
- D. Variable  $\text{SiO}_2$
- E. Variable  $\text{SiO}_2$ ; constant 2%  $\text{LiBO}_2$
- F. Variable  $\text{SiO}_2$ ; constant 2%  $\text{LiBO}_2$  and 0.4%  $\text{NH}_4\text{F}$
- G. Variable  $\text{SiO}_2$ ; constant 2%  $\text{LiBO}_2$  and 0.8%  $\text{NH}_4\text{F}$

TABLE I

Effects of Al, Ca, Fe, and Mg on Titanium Absorption

Matrix	Absorbance
50 µg/ml Ti Standard*	0.117
50 µg/ml Ti Standard* + 1000 µg/ml Fe	0.114
" + 1000 µg/ml Al	0.117
" + 1000 µg/ml Ca	0.102
" + 1000 µg/ml Mg	0.104
" + 500 µg/ml Ca + 500 µg/ml Fe	0.102
" + 500 µg/ml Mg + 500 µg/ml Fe	0.104
" + 500 µg/ml Ca + 500 µg/ml Al	0.114
" + 500 µg/ml Mg + 500 µg/ml Al	0.117

\*50 µg/ml Ti Standard containing 2%  $\text{LiBO}_2$ , 0.1%  $\text{SiO}_2$ , 0.8%  $\text{NH}_4\text{F}$  and 10% HCl.

Effects of interference of major elements normally encountered in iron ores (Ca, Fe, Al, and Mg) were studied. Standard solutions of 50  $\mu\text{g/ml}$  Ti containing 2%  $\text{LiBO}_2$ , 0.1%  $\text{SiO}_2$ , and 0.8%  $\text{NH}_4\text{F}$  were spiked with these elements to obtain concentrations of 1000  $\mu\text{g/ml}$  (equal to 25% in the original sample when processed as per recommended analytical procedure). The results are shown in Table I. Iron and Al did not cause any significant interference while Ca and Mg depressed the signal. Addition of aluminum to the samples however restored the signal. The concentration of Al should exceed the combined concentrations of Ca and Mg. In most iron ores, Al present in the samples will be sufficient to suppress the interferences due to Ca and Mg. For samples unusually high in Ca and Mg and low in Al,  $\text{AlCl}_3$  should be added to the sample solution. A 1000  $\mu\text{g/ml}$  concentration of Al should be adequate for most samples. No addition of Al to standards is necessary, since the purpose of the addition of Al is only to restore the signal depression, caused by Ca and Mg.

#### ANALYTICAL PROCEDURE

Mix 0.2 g of sample and 1 g of lithium metaborate and fuse in a preignited graphite crucible for 15 minutes. Magnetite concentrates and  $\text{TiO}_2$  resist fusion and the melt will adhere to the crucible. In this case, the use of 0.1 g of sample and 0.1 g of finely pulverized silica and a longer fusion time will allow complete fusion of the sample. Let the crucible cool and using forceps drop the globule into a 50-ml test tube containing exactly 50 ml of 10% HCl. If it is necessary to add aluminum to the samples,  $\text{AlCl}_3$  can be added to the dilute acid. Drop a magnet into the test tube and stir on a magnetic stirrer hot plate, using an aluminum block drilled to hold the test tubes. The globule will dissolve in a few minutes. Let the test tube cool and add 0.4 g of ammonium fluoride. Shake and analyze by atomic absorption.

We have found a continuous shift in the standard curve, even within a few minutes time. For best precision we run a 50  $\mu\text{g/ml}$  reference standard between samples and average the absorbance of the reference standards preceding and following a sample. This average is used to correct the absorbance values of standards and samples to a common basis, e.g., the first absorbance reading of the 50  $\mu\text{g/ml}$  reference standard. This will eliminate errors due to short term fluctuations of the slope of the standard curve.

#### PREPARATION OF STANDARDS

Standards may be prepared either by (1) dissolution of titanium metal in HCl or HF and oxidation by dropwise addition of  $\text{HNO}_3$  or (2) fusion of  $\text{TiO}_2$  + added  $\text{SiO}_2$  in  $\text{LiBO}_2$  as described under analytical procedure, or (3) use of U.S.G.S. analyzed rocks, BCR-1, AGV-1, GSP-1 and G-2. Method 3 was found to be most convenient. For example, three or four fusions are made of BCR-1 and processed exactly as the samples, and combined for use as a standard. A standard curve drawn from U.S.G.S. rocks G-2, GSP-1, AGV-1 and BCR-1 gave a perfect straight line and covered a range up to 2.23%  $\text{TiO}_2$ . Since these rocks contain silica and alumina, any interferences due to silica and alkaline earth metals is eliminated. Thus they are ideal standards for the determination of Ti in iron ores or rocks. All standards should contain 2%  $\text{LiBO}_2$ , 0.1%  $\text{SiO}_2$  and 0.8%  $\text{NH}_4\text{F}$ . The solution of  $\text{SiO}_2$  is prepared by fusion and dissolution of finely ground silica using the same procedure as for the samples. This solution is used as needed in making standard solutions. The ammonium fluoride

should be added to samples or standards on the day of analysis; otherwise a gelatinous precipitate results on standing for a few days.

#### PRECISION AND ACCURACY

During the analysis of low grade magnetic iron ores, one sample was analyzed repeatedly over a period of two months. Table II gives the results. The precision, as shown by the coefficient of variation is very good. The mean value agrees very well with the analysis done by a spectrophotometric method by an independent laboratory.

TABLE II  
Precision and Accuracy of the Analytical Procedure

Atomic Absorption Analysis % Ti	% Ti Mean	S.D.	% C.V.	Spectrophotometric Analysis % Ti
1.87, 1.74, 1.82, 1.76				
1.76, 1.77, 1.83	1.78	0.06	3.3	1.78
1.84, 1.76, 1.85				1.80
1.85, 1.75, 1.66, 1.76				
1.84, 1.68, 1.72				

Table III shows a comparison of the average analysis of U.S.G.S. Standard rock samples as reported by Flanagan (9) and analysis by atomic absorption. The agreement is considered very good. The standards in this case were prepared by method 1 described above. The analytical procedure as outlined is sufficiently free from interference for use on a routine basis for the determination of  $\text{TiO}_2$  in iron ores.

TABLE III  
 $\text{TiO}_2$  in U.S.G.S. Standard Rock Samples

Sample	% $\text{TiO}_2$		
	Average Flanagan (9)	Atomic Absorption	
G-2	0.53	0.50	0.53
GSP-1	0.69	0.65	0.69
AGV-1	1.08	1.08	1.06
BCR-1	2.23	2.21	2.25

#### ACKNOWLEDGMENT

The author wishes to thank Dr. Earl H. Beistline, Dean, College of Earth Sciences and Mineral Industry, and Dr. Ernest N. Wolff, Associate Director, Mineral Industry Research Laboratory, for their encouragement and interest in the project.

Received December 20, 1971

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