Determination of Antimony in Lead-Antimony Alloys by Atomic Absorption Spectroscopy Using Indium as an Internal Standard

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A rapid, precise analytical method has been developed by the United States Department of the Interior, Bureau of Mines, for the determination of antimony in lead-antimony alloys. The alloy (0.10 to 30.0 wt.% Sb) is rapidly dissolved in a 10% volume nitric acid solution containing ~5 g of tartaric acid. Antimony is determined by atomic absorption using indium as an internal standard. The relative standard deviation for this internal standard method, based on the analysis of three National Bureau of Standards (NBS) Standard Reference Materials, is approximately 0.50%; an improvement over conventional atomic absorption and a volumetric method by a factor of 5 to 8. The internal standard procedure gives values that are in better agreement with the NBS certified values than analyses using the alternative methods. Analytical time required is less than 30 min.

Index Headings: **Analysis, for antimony; Atomic absorption, internal standard; Methods, analytical.**

INTRODUCTION

This research was conducted as part of the United States Department of the Interior's Bureau of Mines program to develop technology for conserving the Nation's mineral and metal supply through recovery of valuable constituents from waste materials. As part of its secondary metals program, the Bureau of Mines is conducting bench-scale tests on various methods for separating antimony from lead alloys and recovery of the two purified metals. An analytical method for the rapid, accurate determination of antimony in lead alloys at concentrations ranging from 0.10 to 30.0 wt.% antimony is required for an effective metallurgical research program. Prior to the development of this internal standard method, a tedious ASTM method[1] was employed. This report describes the development and evaluation of an internal standardization atomic absorption procedure.

I. ANALYTICAL PROCEDURE

A. Reagents. All reagents were ACS grade. All atomic absorption standards were prepared by dilution of 1000 ppm commercially prepared standards. Tartaric acid purchased from Fisher Scientific* complexed the antimonic acid so that the antimony was completely dissolved in nitric acid. Dissolution of the antimony was not achieved using an older bottle of tartaric acid purchased from another supplier. No tests were conducted to determine the reason for this difference in response. Therefore, the tartaric acid must be checked before use of this suggested analytical procedure.

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* Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

B. Apparatus. A Jarrell-Ash model 82-810 dual channel atomic absorption spectrophotometer was used for all measurements. The use of a dual channel instrument has been shown by other researchers[2,3] to improve accuracy and precision and will not be detailed in this report. The spectrophotometer was operated in the channel A/channel B mode, which allows simultaneous readings of the analytical and reference spectral lines. As operation of the spectrophotometer in the internal standard (A/B mode) may vary with manufacturer and model, it is advised that specific instructions of the manufacturer be followed. For the instrument used in this report, the absorbance of the B channel must fall between 0.5 and 0.7 absorbance unit.

Primary parameters as set by the manufacturers were followed except for antimony. The secondary wavelength for antimony of 231.2 nm was used in order to avoid a spectral interference with the primary wavelength of 217.0 nm for lead.

C. Analytical Procedure. Depending on expected antimony concentration, a 1- to 3-g sample is weighed to the nearest 0.1 mg and placed in a 250-ml beaker. Approximately 50 ml of distilled water is added. Approximately 5 g of tartaric acid is added, and the beaker is swirled to dissolve the acid. Five milliliters of concentrated HNO_3 is added and then the sample is heated on a hot plate for 10 to 15 min to complete dissolution. The sample is quantitatively transferred to a 250-ml volumetric flask. Ten milliliters of concentrated HNO_3 is added and the sample is brought to volume with distilled water.

Standards are prepared as 0, 10, 20, 30, and 40 ppm of antimony. To meet the requirement of channel B falling between 0.5 and 0.7 absorbance unit, the concentration of indium in the antimony standards and the analytical solution is 100 ppm. When further dilution of samples is required, the indium concentration is adjusted to 100 ppm. The spectrophotometer is prepared for operation in the A/B mode. This is achieved by auto zeroing, using distilled water on channel A and then channel B. Channel B, used to measure indium's absorbance, is checked to verify that the absorbance of 100 ppm indium falls between 0.5 and 0.7 unit. Next, the spectrophotometer is switched to the A/B mode and auto-zeroed on the 0 ppm antimony standard. After these steps are completed, the standard curve is derived and the ratio absorbance of the samples is read. The concentration of antimony is calculated from the standard curve plotted as ratio absorbance vs concentration antimony.

II. EXPERIMENTAL

A. Dissolution. Several acid combinations were tried

for the rapid dissolution of the alloy. Hydrochloric acid (HCl) would dissolve the alloy, but the final acid concentration necessary to keep lead and antimony in solution was too great for use in atomic absorption. Standards had to be prepared to match each sample in acid concentration because of the depressant effect of HCl on antimony absorbance.[4] The technique of standard additions was not practical because it required tedious preparation before aspiration. Nebulizer corrosion was also apparent after several aspirations of the high HCl concentration.

Ten percent HNO_3 leaves a white precipitate of antimonic acid. The antimonic acid is soluble in 1:1 HCl, but the problems stated in the preceding paragraph were still present. However, tartaric acid added prior to the addition of HNO_3 alleviated the need for hydrochloric acid through the formation of a soluble tartaric-antimonic acid complex.[5] The dissolution proceeded rapidly and to completion without any complications.

B. Internal Standard. Except for the alkali and alkaline earth elements, no general rules exist for selecting a good internal standard.[3] It has been shown[3] that acetylene (C_2H_2) flow rate, hollow cathode lamp current, and anion species all affect absorbance for many elements. Therefore, three elements that are not normally present in lead-antimony alloys, bismuth, indium, and nickel, were chosen for testing.

An absorbance curve was established for the three internal standard candidates and antimony by first varying the C_2H_2 flow rate. During this test, the current of each hollow cathode lamp was set to manufacturer's specifications. Fig. 1 is a comparison of the absorbance patterns. Condition A is a stoichiometric flame, condition B is a lean flame, and condition C is a fuel-rich flame. Flame conditions were controlled from one element to the next to ensure that the proper fuel/air ratio was constant in each condition for each element tested. Indium showed the greatest similarity of absorbance pattern to antimony's and was chosen for further testing.

Hollow cathode lamp current was varied, and the resulting absorbance curves appear in Fig. 2. The two elements show essentially the same absorbance pattern as the current was increased to the manufacturer's maximum. Each hollow cathode lamp was warmed up for 10 min before testing.

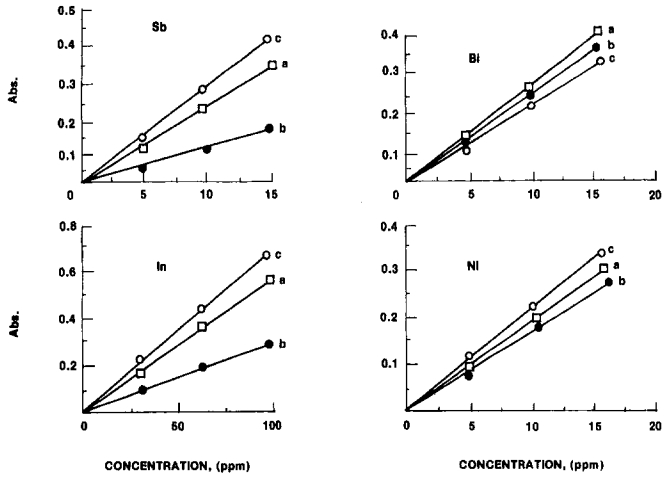

FIG. 1. Variation of absorbance with acetylene pressure.

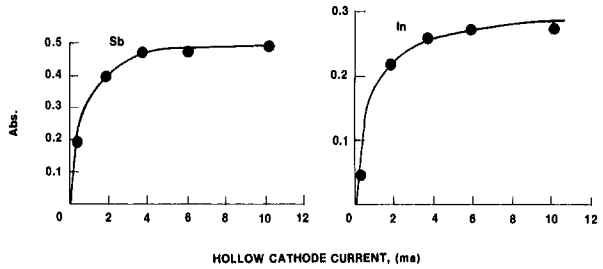

FIG. 2. Variation of absorbance with hollow cathode current.

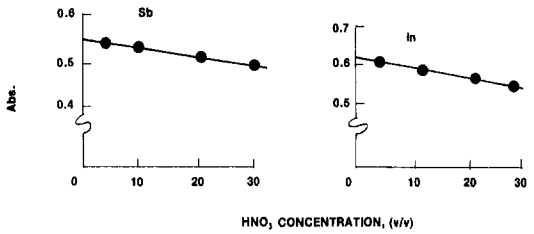

FIG. 3. Variation of absorbance with HNO_3 concentration.

TABLE I. Comparison of certified NBS and internal standard values for antimony.

Sample	Antimony (wt. %)	
	NBS certified	Bureau of Mines internal standard
NBS 53d	9.93	9.94 ± 0.04
NBS 54c	7.27	7.25 ± 0.04
NBS 124b	0.20	0.198 ± 0.002

TABLE II. Comparison of ASTM Method E-57 and internal standard values for antimony.

Sample	Antimony (wt. %)			
	ASTM E-57	R.S.D.[a]	Internal standard	R.S.D.
NBS 53d	10.04 ± 0.19	1.89	9.94 ± 0.04	0.40
Ingot S-65	22.5 ± 0.86	3.82	22.4 ± 0.10	0.45

[a] Relative standard deviation (%).

TABLE III. Comparison of atomic absorption values for antimony with and without indium as an internal standard.

Sample	With internal standard	R.S.D.[a]	Without internal standard	R.S.D.
NBS 53d	9.94 ± 0.04	0.40	10.1 ± 0.27	2.67
NBS 54c	7.25 ± 0.04	0.55	7.08 ± 0.24	3.39
NBS 124b	0.198 ± 0.002	1.01	0.142 ± 0.010	7.04
Ingot S-65	22.4 ± 0.10	0.45	22.6 ± 0.47	2.09

[a] Relative standard deviation (%).

Finally, the effect that HNO_3 concentration had on both antimony and indium absorbance was measured. Fig. 3 shows that for less than 20% nitric acid concentration, the two elements show only a slight depression in absorbance. The results of these three tests indicated that indium would be a viable internal standard for the determination of antimony.

III. RESULTS AND DISCUSSION

Three National Bureau of Standards (NBS) Standard Reference Materials along with a lead-antimony alloy ingot were treated as detailed in the analytical procedure.

The standard reference materials chosen were: NBS 53d—a lead-bearing alloy similar to the type of samples being submitted for analysis; 54c—a tin-bearing metal; and NBS 124b—a copper matrix metal.

Table I compares the average of 10 independent determinations for antimony of each NBS material to the certified NBS values. The internal standard values of 9.94, 7.25, and 0.198 wt.% agree excellently to the respective certified NBS values of 9.93, 7.27, and 0.20 wt.%. Ingot S-65, a typical lead-antimony alloy and NBS 53d were analyzed by ASTM E-57; these results were compared with the internal standard result. Table II shows good agreement between the two methods; however, the internal standard results are 5 to 8 times more precise than those by the ASTM method. Table III is a comparison of results obtained by atomic absorption with and without internal standardization. Not only is precision increased by a factor of 6 with internal standardization, but also the results obtained using an internal standard compare more favorably with the certified NBS values. Each result reported in Tables II and III was obtained by averaging 10 independent determinations for antimony.

IV. CONCLUSION

The results obtained using tartaric-nitric acid dissolution followed by determination of antimony by atomic absorption using indium as an internal standard are more precise and accurate than either of the two alternative analytical methods.

Analysis of three NBS standard reference materials, 53d, 54c, and 124b, showed excellent agreement with the certified values for antimony. The internal standard method should be applicable to other matrices as is indicated by the excellent agreement obtained for antimony in NBS 54c and 124b.

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Calcium Isotope Effects in Atomic Absorption

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Measurements are reported for the absorption of the 422.7 nm line of a natural-abundance calcium hollow cathode lamp by solutions of ^{40}Ca, ^{44}Ca, and ^{48}Ca at 0.5 to 3.0 ppm levels in 0.06 *M* HCl (aqueous) when aspirated into air-acetylene and nitrous oxide-acetylene flames. In the case of the air-acetylene flame the relative absorptions per mole of calcium in solution were 1.00, 1.11, and 1.08 for the 40, 44, and 48 isotopes, respectively. With the nitrous oxide-acetylene flame similar experiments gave ratios of 1.00, 1.08, and 1.06 in the same order. These results may be rationalized with a model that considers the simultaneous effects of isotope shifting, Lorentz broadening and shifting, and Doppler broadening of the calcium resonance line in the flame. With the air-acetylene flame, solutions that also contained 5000 ppm of Sr as $SrCl_2$ gave relative absorbances for the 40, 44, and 48 calcium isotopes of 1.00, 1.04, and 1.10. Flame-atomic-distribution studies lead to the conclusion that in the presence of 5000 ppm of Sr, calcium kinetic isotope effects are also important.

Index Headings: **Calcium atomic absorption; Calcium isotope effects; Spectral line broadening.**

INTRODUCTION

As part of a research program aimed at determining the equilibrium constants for isotope-exchange reactions, the need arose to analyze small amounts of isotopically pure aqueous solutions containing ^{40}Ca, ^{44}Ca, and ^{48}Ca. Our desire to evaluate the utility of atomic absorption in this context prompted the investigations reported here.

I. EXPERIMENTAL

A. Materials. The calcium isotopes, supplied as calcium carbonates, were purchased from the Oak Ridge National Laboratory. According to the spectrographic analyses that accompanied the samples, the chemical purity of each of the calcium carbonates exceeded 99.3%. For ^{40}Ca, ^{44}Ca, and ^{48}Ca the reported isotopic purities were greater than 99.9%, 98%, and 96%, respectively.

Because it is common practice to use large excesses of strontium or lanthanum as releasing agents[1] when, in particular, biological or geological samples are assayed for calcium using an air-acetylene flame, some of the solutions of the calcium isotopes we studied in this flame also contained strontium chloride (as $SrCl_2 \cdot 6H_2O$ certified < 2 μg of Mg per mg, J. T. Baker Chemical Co.) at a final concentration of 5000 μg of Sr per ml. To minimize calcium contamination, $SrCl_2 \cdot 6H_2O$ was reprecipitated from a saturated aqueous solution at 75°C using anhydrous ethyl alcohol. The precipitate was collected, washed with alcohol, and vacuum dried. The purified material was found to contain 0.00011% by weight calcium contamination, so that the 5000 μg of Sr per ml

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