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The Atomic Absorption Spectrophotometric Determination of Bismuth in Premixed Inert Gas(Entrained Air)-Hydrogen Flames

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The atomic absorption spectrophotometric determination of bismuth in aqueous solutions was established in premixed inert gas(entrained air)-hydrogen flames with a "multi-flame" burner in conjunction with a Nippon Jarrell-Ash Model AA-1 atomic absorption/flame emission spectrophotometer. Under the optimum operating conditions, a straight calibration graph was obtained at 223.1 nm in the concentration range of 0–10 ppm and the bismuth sensitivity for a 1% absorption was 0.1 ppm. The effects of acids and other elements on the bismuth atomic absorption were examined. Phosphoric acid caused a considerable depressing effect on the bismuth absorption. Hydrochloric acid remarkably depressed the bismuth absorption at acid concentrations lower than 0.5 N, but it gave no interference in acid concentrations higher than 0.5 N, in which water-insoluble bismuth oxychloride was quickly dissolved in hydrochloric acid. Hydrofluoric, nitric, perchloric, and sulfuric acids had no effect on the bismuth absorption. Most of the elements examined, with the exception of aluminum, boron, cerium, silicon, and zirconium, gave no interference to the bismuth absorption. The depressing interferences due to some elements were removed in appearance by adding a large amount (2000 ppm) of magnesium (as chloride). Furthermore, it was found that most of the depressing interferences could be eliminated by adding a large amount (0.1 M) of ammonium salts (as chloride or perchlorate) to the sample solutions. Bismuth in the presence of magnesium chloride, ammonium chloride, or ammonium perchlorate could be determined without interference from various other elements. The atomic absorption spectrophotometric method was applied to the determination of bismuth in sulfide ores, aluminum-, tin-, and lead-base alloys with satisfactory results.

Bismuth is determined readily in an air-acetylene flame. The bismuth line at 306.8 nm is of limited usefulness, however, because it falls on the band head of the major hydroxyl band in the flame; moreover, the flame luminosity makes the atomic absorption measurement uncertain. The resonance line at 223.1 nm is usually the most useful. The best sensitivity for a 1% absorption in the determination of bismuth in an aqueous solution by atomic absorption spectrophotometry with an air-acetylene flame is 0.7 ppm at the 223.1 nm line.[1] Kinser[2] has reported the determination of bismuth in biological samples with an air-acetylene flame without any interference from the materials found in the samples. Bismuth could be readily extracted from aqueous solutions into organic solvents with such chelating agents as ammonium pyrrolidine dithiocarbamate (APDC), dithizone, etc. An APDC-organic solvent extraction system has been used in the analysis of urine samples[3] and the lead-base and tin-base metals.[4] The dithizone-carbon tetrachloride system has been used in the determination of bismuth in ferrous alloys.[5] Furthermore, Headridge and Richardson[6] have reported on the use of a bismuth iodide-methyl isobutyl ketone system for the determination of bismuth in ferrous alloys. On the other

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[1] W. Slavin, "Atomic Absorption Spectroscopy," Interscience Publishers, New York, N. Y. (1968), p. 60.

[2] R. E. Kinser, *Amer. Ind. Hyg. Assoc. J.*, **27**, 260 (1966).

[3] J. B. Willis, *Anal. Chem.*, **34**, 614 (1962).

[4] H. K. Y. Lau, H. A. Droll, and P. F. Lott, *Anal. Chim. Acta*, **56**, 7 (1971).

[5] G. Kisfaudi and M. Lenhof, *ibid.*, **55**, 444 (1971).

[6] J. B. Headridge and J. Richardson, *Analyst* (London), **95**, 930 (1970).

hand, McGee and Winefordner[7)] have described the determination of bismuth using a modified long-path absorption cell and a xenon lamp as a continuum radiation source, with an argon-hydrogen flame. Burke[8)] has studied the scavenger property of manganese (IV) oxide for the separation of less than 100 ppm of bismuth by atomic absorption spectrophotometry with an air-acetylene flame.

Several authors have examined the so-called "cool" flames with respect to their use in flame methods of analysis. These flames are usually entrained air-hydrogen flames in which the combustible gas is diluted with an inert gas, such as nitrogen or argon. Winefordner *et al.*[9,10)] have used an argon (entrained air)-hydrogen flame in the flame-emission spectrophotometric determination of 14 elements and have obtained limits of detection which are better than, or as good as, those obtained with an oxygen-hydrogen flame. Their success has been attributed to the low background noise associated with the argon-hydrogen flame and also to possible chemiluminescence with certain elements. Dagnall *et al.*[11)] have used a hydrogen flame diluted with nitrogen to observe the molecular band emission of S_2 in the determination of sulfur. The argon (entrained air)-hydrogen flame has also been used in atomic absorption spectrophotometry because of its low flame background absorption in the ultraviolet region; this has resulted in improving the atomic absorption sensitivities for several elements.[12)]

This paper will decribe an investigation of the flame characteristics for bismuth in the premixed argon (entrained air)- and nitrogen(entrained air)-hydrogen flames produced using a specially-constructed "multi-flame" burner,[13)] and an investigation of the interference with bismuth atomic absorptions. A depressing interference was observed over a wide range of concentration of several elements. It may, however, be noted that a large amount of magnesium can eliminate the depressing effect due to some of the elements examined. This was successfully applied to the determination of bismuth in several metallurgical samples.

Experimental

Apparatus. All the atomic absorption measurements were performed using a Nippon Jarrell-Ash Model AA-1 atomic absorption/flame emission spectrophotometer on a single-pass system. A "multi-flame" burner[13)] was used in conjunction with a Techtron standard nebulizer-chamber. The height in the flame was taken as zero when the light beam from the hollow-cathode lamp just touched the top of the burner head. The analytical wavelength was 223.1 nm, and the light source was a bismuth high-spectral-output hollow-cathode lamp (Westinghouse, Type No. 45467), operated at 8 mA. The gas flow rates were carefully regulated and were monitored on calibrated flow meters.

Reagents. A stock solution of bismuth (1000 ppm) was prepared by dissolving 1.000 g of high-purity bismuth metal in 10 ml of concentrated nitric acid by gentle heating, and by then diluting it to 1000 ml with distilled water. It was necessary to keep the acid concentration high enough (pH 1) to prevent its hydrolysis. Lower concentrations of standard bismuth solutions were freshly prepared daily by diluting the stock solution.

All the other reagents used were either of a reagent grade or of the highest quality available. Blanks were run on each solution in the case of the interference study with the bismuth atomic absorption.

Results and Discussion

Bismuth Sensitivity in Various Flames. Slavin[1)] and Kinser[2)] have reported a sensitivity of 0.7 ppm for a 1% absorption in aqueous solutions with an air-acetylene flame at the wavelength of the 223.1 nm bismuth resonance line. The bismuth sensitivities for a 1% absorption in aqueous solutions were obtained in several flames produced with a "multi-flame" burner[13)] under optimum flame and measuring conditions. They were 0.14, 0.80, 0.18, 1.00, 0.10, and 0.11 ppm in the premixed air-acetylene, nitrous oxide-acetylene, air-hydrogen, nitrous oxide-hydrogen, argon (entrained air)-hydrogen, and nitrogen(entrained air)-hydrogen flames respectively. The sensitivities in the inert gas(entrained air)-hydrogen flames were considerably better than those obtained in the other hydrogen or acetylene flames. Furthermore, it was found that the inert gas(entrained air)-hydrogen flames gave extremely low background absorptions at the 223.1 nm line compared with the other flames examined. These higher sensitivities indicated that such relatively volatile elements as arsenic, bismuth, cadmium, lead, selenium, tin, and zinc were sufficiently atomized, even in the low-temperature flames.

Effect of Flame Composition and Flame Height. At a fixed flow rate of argon or nitrogen as a nebulizing gas, the hydrogen flow rates were varied from 3.6 to 12.6 l/min and the absorptions were measured for 10 ppm of bismuth in various flame heights in order to find the optimum flame composition and flame height. The results obtained in the argon(entrained air)-hydrogen flame are shown in Fig. 1. It may be seen from Fig. 1 that the bismuth atomic absorption may be depends remarkably on both the flame composition and the flame height. Similar results were obtained in the nitrogen(entrained air)-hydrogen flame. The optimum conditions for bismuth atomic absorption are summarized as follows. Argon(entrained air)-hydrogen flame: hydrogen flow rate, 5.4 l/min; argon flow rate, 4.5 l/min; argon pressure, 1.5 kg/cm^2; height in the flame, 4 mm above the top of burner head. Nitrogen(entrained air)-hydrogen flame: hydrogen flow rate, 5.4 l/min; nitrogen flow rate 5.0 l/min; nitrogen pressure, 1.5 kg/cm^2; height in the flame,

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7) W. W. McGee and J. D. Winefordner, *Anal. Chim. Acta*, **37**, 429 (1967).

8) K. E. Burke, *Anal. Chem.*, **42**, 1536 (1970).

9) K. Zacha and J. D. Winefordner, *Anal. Chem.*, **38**, 1539 (1966).

10) C. Veillon, J. M. Mansfield, M. L. Parsons, and J. D. Wineforder, *ibid.*, **38**, 204 (1966).

11) R. M. Dagnall, K. C. Thompson, and T. S. West, *Analyst* (London), **92**, 506 (1967).

12) H. L. Kahn and J. E. Schallis, *At. Absorption Newslett.*, **7**, 5 (1968).

13) T. Nakahara, H. Date, M. Munemori, and S, Musha, This Bulletin, **46**, 637 (1973).

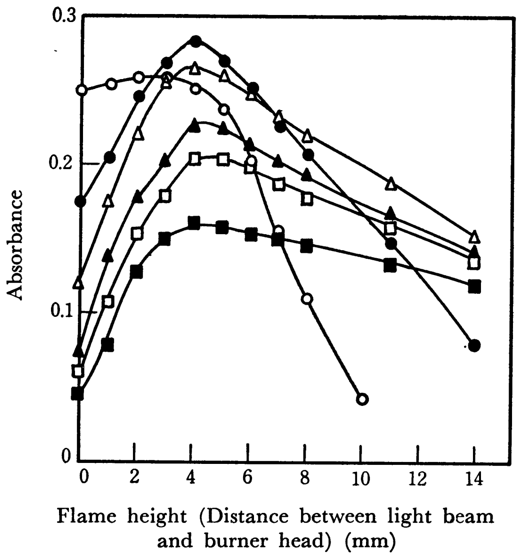

Fig. 1. Effect of flame composition and flame height on bismuth atomic absorption. Concentration of bismuth: 10 ppm.
Flame: an argon(entrained air)-hydrogen flame.
Hydrogen flow rate: (○) 3.6 l/min; (●) 5.4 l/min; (△) 7.2 l/min; (▲) 9.0 l/min; (□) 10.8 l/min; (■) 12.6 l/min.

5 mm above the top of the burner head. Under these conditions, both the flames were completely invisible and quiet.

Effect of Acids. No detailed study has been previously reported on the effect of acids on the determination of bismuth by atomic absorption spectrophotometry in either an air-acetylene flame or an air-hydrogen flame. The bismuth absorptions were, therefore, measured in inert gas(entrained air)-hydrogen, flames for 10 ppm of bismuth in the presence of acids, the concentrations of which were varied from 0.1 to 2.0 N. The acids examined included hydrochloric, hydrofluoric, nitric, phosphoric, perchloric, and sulfuric acids. The results obtained in the argon(entrained air)-hydrogen flame are shown in Fig. 2. Similar results were obtained in the nitrogen(entrained air)-hydrogen flame. Phosphoric acid had a considerable depressing effect on the bismuth atomic absorption. The effect of phosphoric acid may be due to the difficulty of the thermal decomposition of the phosphate in the low-temperature flame. On the other hand, hydrofluoric, perchloric, and sulfuric acids caused a slight enhancement of the bismuth atomic absorption.

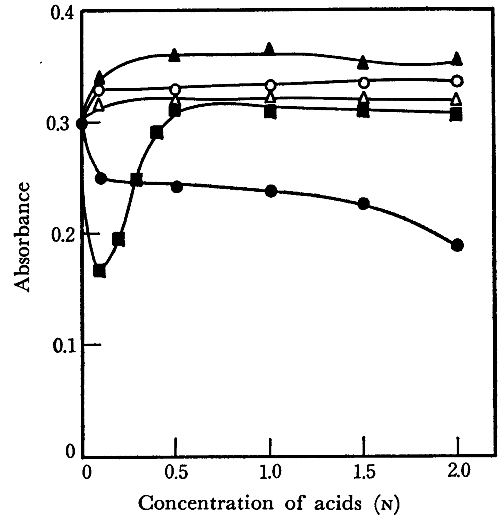

Fig. 2. Effect of acids on bismuth atomic absorption. Concentration of bismuth: 10 ppm. Flame: an argon(entrained air)-hydrogen flame. (▲) Perchloric acid; (○) hydrofluoric and sulfuric acids; (△) nitric acid; (■) hydrochloric acid; (●) phosphoric acid.

Hydrochloric acid was found, as is shown in Fig. 2, to depress remarkably the bismuth atomic absorption in acid concentrations lower than 0.5 N, but this depressing interference disappeared in acid concentrations higher than 0.5 N because water-insoluble bismuth oxychloride is quickly dissolved in hydrochloric acid of a higher concentration. The bismuth solution containing hydrochloric acid at the 1.0 N level was used in all the later work, because the effect of hydrochloric acid caused the smallest interference in the determination of bismuth of all the acids examined.

Effect of Various Other Elements. Winefordner *et al.*[9,10] have described that an argon(entrained air)-hydrogen flame was useful for atomic fluorescence and flame emission spectrophotometry. Kirkbright and Ranson[14] have reported that the determination of some elements, such as arsenic and selenium, in the argon(entrained air)-hydrogen flame suffered from interference from foregin elements because of the inability of the cool flame to vaporize or atomize the other elements present in the sample solution.

The effects of various other elements on the atomic absorption spectrophotometric determination of bismuth were studied in detail at constant concentration levels: aqueous solutions containing 10 ppm of bismuth and 200 ppm of other elements. The results obtained in both the flames are shown in Table 1. Most elements, with the exception of aluminum, beryllium, silicon, etc., gave no interference, the deviation of the absorbance of bismuth being less than 5%. As is shown in Table 1, however, aluminum, beryllium, boron, cerium, silicon, and zirconium, which easily produce refractory metallic oxides in the flame, depressed the bismuth atomic absorption. These depressing effects on the bismuth absorption can not be satisfactorily explained.

Because the flame composition has been shown to be an important parameter in interference studies,[1,15,16] the hydrogen-flow rate and the flame height in inert gas(entrained air)-hydrogen flames were varied to see what effect, if any, would be thus produced on the depressing interference. For example, an aluminum depression showed a dependency on these parameters. As is shown in Fig. 3, this interference could be negative

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[14] G. F. Kirkbright and L. Ranson, *Anal. Chem.*, **43**, 1238 (1971).

[15] J. A. Dean and T. C. Rains, "Flame Emission and Atomic Absorption Spectrometry," Vol. 1, Marcel Dekker, New York, N. Y. (1969).

[16] R. Herrman and C. Th. J. Alkamade, "Chemical Analysis by Flame Photometry," 2nd. revised ed., Interscience Publishers, New York, N. Y. (1963).

Table 1. Effect of other elements on bismuth atomic absorption

	Argon(entrrained air)-hydrogen flame	Nitrogen(entrained air)-hydrogen flame
No interference	Ag$^{a)}$, As$^{b)}$, Au$^{c)}$, Ba$^{a)}$, Ca$^{a)}$, Cd$^{a)}$, Co$^{c)}$, Cr$^{c)}$, Cu$^{d)}$, Fe$^{c)}$, Hg$^{c)}$, In$^{c)}$, K$^{c)}$, La$^{c)}$, Li$^{c)}$, Mg$^{c)}$, Mn$^{a)}$, Mo$^{e)}$, Na$^{c)}$, Ni$^{d)}$, Pb$^{a)}$, Rb$^{c)}$, Sb$^{c)}$, Se$^{b)}$, Sn$^{c)}$, Sr$^{a)}$, Te$^{b)}$, Ti$^{c)}$, Tl$^{a)}$, V$^{e)}$, W$^{b)}$, Y$^{a)}$, Zn$^{a)}$	Ag$^{a)}$, As$^{b)}$, Au$^{c)}$, Ba$^{c)}$, Cd$^{a)}$, Cu$^{d)}$, Fe$^{c)}$, Hg$^{c)}$, In$^{c)}$, K$^{c)}$, La$^{c)}$, Li$^{c)}$, Mg$^{c)}$, Mn$^{a)}$, Mo$^{e)}$, Na$^{c)}$, Pb$^{a)}$, Sb$^{d)}$, Se$^{b)}$, Sn$^{c)}$, Te$^{b)}$, Ti$^{c)}$, Tl$^{a)}$, V$^{e)}$, W$^{b)}$, Y$^{a)}$, Zn$^{a)}$
Depression	Al$^{c)}$, B$^{f)}$, Be$^{d)}$, Ce$^{d)}$, Cs$^{c)}$, Pd$^{c)}$, Si$^{b)}$, Zr$^{a)}$	Al$^{c)}$, B$^{f)}$, Be$^{d)}$, Ca$^{a)}$, Ce$^{d)}$, Co$^{c)}$, Cr$^{c)}$, Cs$^{c)}$, Ni$^{d)}$, Pd$^{c)}$, Si$^{b)}$, Sr$^{a)}$, Zr$^{a)}$
Enhancement	None	None

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

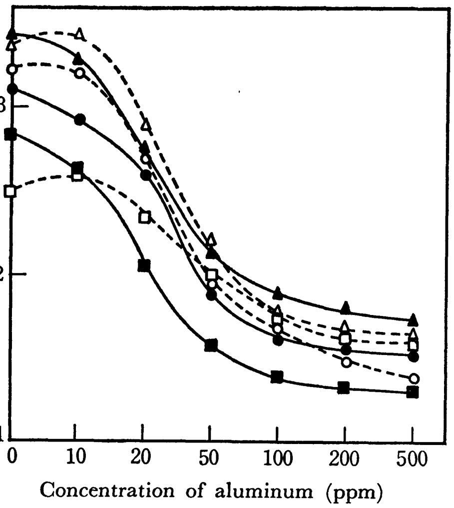

Fig. 3. Effect of hydrogen flow rate and flame height on the interference from aluminum with bismuth atomic absorption. Concentration of bismuth: 10 ppm. Flame: an argon(entrained air)-hydrogen flame.
Effect of hydrogen flow rate: (■) 4.5 l/min; (▲) 5.4 l/min; (●) 6.3 l/min. Effect of flame height above burner head: (○) 2 mm; (△) 4 mm; (□) 8 mm.

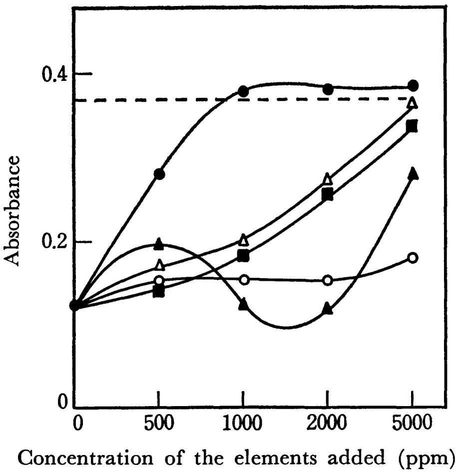

Fig. 4. Effect of non-interfering elements on the depressing interference from aluminum. Concentration of bismuth: 10 ppm. Concentration of aluminum: 2000 ppm. Flame: an argon(entrained air)-hydrogen flame. ---- Bismuth alone; (●) magnesium; (△) yttrium; (■) lanthanum; (▲) potassium; (○) mercury.

or occasionally positive, depending on the hydrogen flow rate and the flame height. This phenomenon can not be explained adequately, but it is possibly due to a perturbation of basic flame chemistry or it is possibly related to the specific chemistry of the elements and bismuth in the flame.

On the other hand, no element was found to enhance the bismuth atomic absorption.

Effect of Magnesium on the Depressing Interference. The depressing interference described above depends considerably on the concentration of the depressing elements, the flame composition, and the flame height. In an attempt to eliminate the depressing interference due to aluminum, beryllium, *etc.*, the effect of the further addition of such an element as gave no interference with the bismuth absorption, *i. e.*, mercury, potassium, lanthanum, magnesium, and yttrium, was examined on a bismuth solution containing interferents. The results on the aluminum interference are shown in Fig. 4. As is shown in Fig. 4, magnesium was the most effective in eliminating the depressing interference among the elements examined. Then, the bismuth (10 ppm) absorptions were measured in the presence

Table 2. Effect of magnesium on the depressing interference

Element	Relative absorbance			
	Argon(entrained air)-hydrogen flame		Nitrogen(entrained air)-hydrogen flame	
	In the absence of magnesium	In the presence of magnerium	In the absence of magnesium	In the presence of magnesium
None	1.00	1.00	1.00	1.00
Al	0.43	1.03	0.37	1.03
B	0.41	1.06	0.60	1.05
Be	0.62	1.07	0.59	1.05
Ca	0.96	1.06	0.76	1.05
Ce	0.43	0.45	0.16	0.25
Co	1.02	1.00	0.86	1.05
Cr	1.00	1.00	0.54	1.05
Cs	0.62	1.04	0.62	1.03
Ni	0.95	1.00	0.74	1.01
Pd	0.69	0.97	0.47	0.98
Si	0.42	1.06	0.26	1.04
Sr	0.97	1.02	0.79	1.01
Zr	0.18	1.05	0.07	1.04

The concentrations of bismuth, the elements added, and magnesium were 10, 200, and 1000 ppm, respectively.

of the depressing elements (200 ppm) with and without the addition of magnesium (as chloride) (1000 ppm). The results obtained in both the flames are shown in Table 2. The interference from all the depressing elements, with the exception of that of cerium, disappeared completely. This phenomenon could be applied to the atomic absorption spectrophotometric determination of bismuth without any interference from matrix elements.

The mechanism of the interference-elimination due to magnesium cannot be satisfactorily explained. If the interference from aluminum in the determination of bismuth is considered to be due to the formation of bismuth aluminate in the flame, the elimination of the interference by adding a large amount of magnesium may be explained in terms of the predominant formation of magnesium aluminate in the flame, resulting in a release of the bismuth atoms from the influence of aluminum.

Effect of the Ammonium Ion on the Interference. As is shown in Table 2, chromium depressed the bismuth absorption in the nitrogen(entrained air)-hydrogen flame, but it did not do so in the argon(entrained air)-hydrogen flame. This fact seemed to be very interesting; therefore, the interference from chromium in the nitrogen(entrained air)-hydrogen flame was studied with various kinds of chromium compounds. The results are shown in Fig. 5. The ammonium salts gave no interference with the bismuth atomic absorption, while the others remarkably depressed the bismuth atomic absorption. This fact indicated that the ammonium ion possibly plays an important role in the elimination of the depressing interference. Further investigation showed that the depressing interference from chromium could be eliminated with the addition of a large amount of ammonium chloride or ammonium perchlorate, as is shown in Fig. 6.

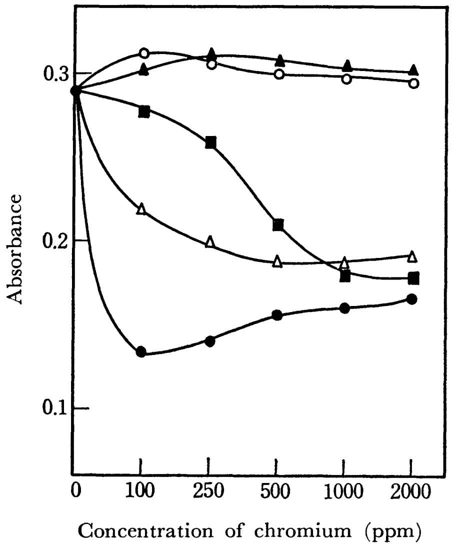

Fig. 5. Effect of chromium compounds on bismuth atomic absorption in the nitrogen(entrained air)-hydrogen flame. Concentration of bismuth: 10 ppm. (▲) Ammonium chromate; (○) ammonium dichromate; (■) potassium chromate; (△) potassium dichromate; (●) chromium(III) chloride.

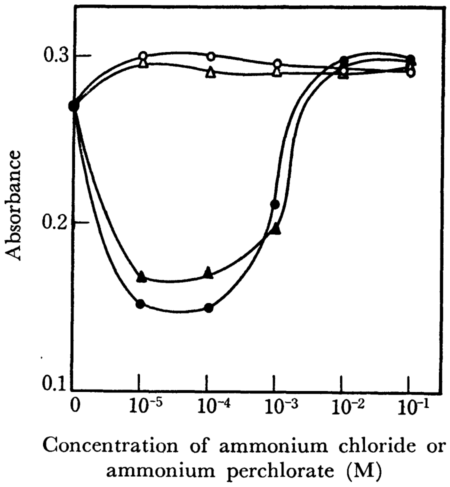

Fig. 6. Effect of ammonium salts on the depressing interference from chromium(III) chloride in the nitrogen (entrained air)-hydrogen flame. Concentration of bismuth: 10 ppm. (○) Ammonium perchlorate alone; (△) ammonium chloride alone; (●) ammonium perchlorate in the presence of chromium(III) chloride (Concentration of chromium: 1000 ppm); (▲) ammonium chloride in the presence of chromium(III) chloride (Concentration of chromium: 1000 ppm).

Then, the atomic absorptions were measured for a solution containing bismuth (10 ppm) and the depressing elements (200 ppm) in the presence of a large amount (0.1 M) of ammonium chloride or ammonium perchlorate in the inert gas (entrained air)-hydrogen flames. The results are shown in Table 3. The interferences from all the depressing elements appeared to disappear completely.

TABLE 3. EFFECT OF AMMONIUM CHLORIDE AND AMMONIUM PERCHLORATE ON THE DEPRESSING INTERFERENCE

Element	Relative absorbance			
	Argon(entrained air)-hydrogen flame		Nitrogen(entrained air)-hydrogen flame	
	In the presence of ammonium chloride	In the presence of ammonium perchlorate	In the presence of ammonium chloride	In the presence of ammonium perchlorate
None	1.00	1.00	1.00	1.00
Al	0.98	1.05	0.95	0.98
B	0.96	1.01	0.95	0.98
Be	0.97	0.99	0.96	0.98
Ca	0.96	0.97	0.95	0.98
Ce	0.94	0.93	0.90	0.95
Co	1.00	1.00	1.02	1.01
Cr	0.99	1.02	1.02	0.98
Cs	0.95	1.02	0.96	0.98
Ni	0.98	1.02	0.99	0.98
Pd	0.95	0.93	0.97	0.92
Si	1.02	1.00	1.05	0.95
Sr	1.02	0.99	0.98	0.98
Zr	1.02	0.97	1.05	0.98

The concentrations of bismuth, ammonium chloride, and ammonium perchlorate were 10 ppm, 0.1 M, and 0.1 M, respectively.

Effects of Organic Solvents. The effects of organic solvents on the bismuth atomic absorption were also examined. A series of primary alcohols were selected, and the concentrations of the alcohols added were from 10 to 50% by volume. The effect of the alcohols was found to be a depressing interference; that is, the bismuth atomic absorption was decreased with an increase in the alcohol concentrations in the sample solutions. A more detailed investigation was not made on the effects of organic solvents.

Calibration Graphs and Sensitivity. Typical calibration graphs for bismuth are shown in Fig. 7. With magnesium or ammonium chloride added, the same graph was obtained in the presence and in the absence of aluminum. The bismuth sensitivities for a 1% absorption were 0.10 and 0.11 ppm in the argon(entrained air)-hydrogen flame and the nitrogen(entrained air)-hydrogen flame respectively.

Application to the Determination of Bismuth in Sulfide Ores, Aluminum-, Tin-, and Lead-base Alloys. On the basis of the above-mentioned observations, the following procedures were followed for determination of bismuth in some practical samples, *e. g.*, sulfide ores, aluminum-, tin-, and lead-base alloys.

Sulfide Ores: A 2.5-g ore sample was weighed and dissolved in about 70 ml of dilute aqua regia by gentle heating on a hot plate. After the solution had then been cooled to room temperature, the insoluble matter was filtered out. The filtrate was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. The final solution was adjusted to provide a concentration of about 1.0 N hydrochloric acid. The major constituents in the ore samples were found spectrographically to be copper, iron, silicon, and lead by means of a d. c. arc technique on a Shimadzu Type GE-340 Ebert mounting emission spectrograph. Furthermore, these elements were determined in a nitrous oxide-acetylene flame by using a Hitachi Model 207 atomic absorption spectrophotometer. As a result, the contents of the sulfide ore sample of A mine were found to be 18.3, 17.9, 14.0, and 3.9% for copper, iron, zinc, and lead respectively. The contents of the sulfide ore sample of B mine were found to be 83.0, 0.3, 0.2, and 0.1% for iron, copper, zinc, and lead respectively. The silicon and sulfur in the samples were separated as silicate and elementary sulfur from the sample solutions by filtration after the dissolution of the samples.

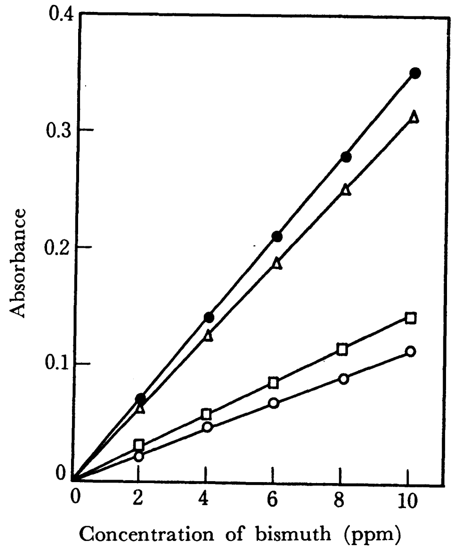

Fig. 7. Calibration graphs for bismuth. Flame: an argon (entrained air)-hydrogen flame. (○) In the presence of aluminum (2000 ppm); (□) in the presence of aluminum (1000 ppm); (●) in the presence of magnesium (2000 ppm) alone, magnesium (2000 ppm) and aluminum (1000 ppm), or magnesium (2000 ppm) and aluminum (2000 ppm); (△) bismuth alone.

Table 4. Results of the determination of bismuth in sulfide ores

Sample	Bismuth content (%)		
	Atomic absorption method		Colorimetric method
	Ar-H_2[a]	N_2-H_2[b]	
A mine ore (Cu conc.)	0.0041[c] 0.0038[d]	0.0044[c] 0.0042[d]	0.0039
B mine ore (S conc.)	0.0068[c] 0.0065[d]	0.0072[c] 0.0064[d]	0.0066

a) Argon(entrained air)-hydrogen flame.
b) Nitrogen(entrained air)-hydrogen flame.
c) Determined by using the calibration graph method.
d) Determined by using the standard addition method.

The bismuth in the ore samples was determined by the standard addition method and by the calibration graph method. Copper, iron, lead, and zinc did not interfere with the determination of bismuth, as has been described above. However, since small amounts of silicon and other interferents were presumably present in the samples, both sample and standard solutions were prepared so as to contain magnesium of 2000 ppm and hydrochloric acid of 1.0 N in the final solutions. The bismuth atomic absorptions were measured at 223.1 nm in the inert gas(entrained air)-hydrogen flames under optimum conditions. The results of the determinations are shown in Table 4. The results were compared with those obtained by the colorimetric method, in which the bismuth contents in sulfide ores were determined by a two-stage extraction with sodium diethyldithiocarbamate into carbon tetrachloride.[17]

Aluminum-base Alloys: As is shown in Fig. 3, the presence of aluminum caused a depressing interference with the bismuth atomic absorption. Therefore, a sufficient amount of magnesium (5000 ppm) was added to the sample solutions in order to eliminate the interference from the matrix element, *i. e.*, aluminum, in the determination of bismuth. A 0.5-g sample was dissolved in 20 ml of aqua regia by gentle heating on a hot plate. After cooling, the sample solution was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. A 10-ml aliquot was taken out, 2.5 ml of a 50000 ppm magnesium solution and 5 ml of 5 N hydrochloric acid were added, and then the mixture was diluted to 25 ml with distilled

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[17] K. Yaguchi and J. Kaneko, *Bunseki Kagaku*, **19**, 705 (1970).

TABLE 5. RESULTS OF THE DETERMINATION OF BISMUTH IN ALUMINUM-, TIN-, AND LEAD-BASE ALLOYS

Sample	Bismuth content (%)		
	Cert. value	Atomic absorption method	
		Ar-H_2[a]	N_2-H_2[b]
Aluminum-base alloy			
No. 1	0.04	0.037[c]	0.043[c]
		0.042[d]	0.045[d]
No. 2	0.05	0.047[c]	0.049[c]
		0.048[d]	0.052[d]
Tin-base alloy			
No. 1	0.028	0.029[c]	0.028[c]
		0.027[d]	0.025[d]
No. 2	0.040	0.041[c]	0.038[c]
		0.038[d]	0.037[d]
Lead-base alloy			
No. 1	0.13	0.13_7[c]	0.13_6[c]
		0.14_0[d]	0.14_2[d]

a) Argon(entrained air)-hydrogen flame.
b) Nitrogen(entrained air)-hydrogen flame.
c) Determined by using the calibration graph method.
d) Determined by using the standard addition method.

water. The resultant solution was sprayed into the flame, and the determination of bismuth was carried out by both the standard addition method and the calibration graph method. The results are shown in Table 5. The results agreed closely with the certificate values.

Tin- and Lead-base Alloys: A 0.9-g sample was dissolved in 30 ml of 6 N acid by slowly heating it on hot plate. The acid employed was hydrochloric acid for tin-base alloys and nitric acid for lead-base alloy. After cooling the sample solution was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. A 10-ml aliquot was taken out and diluted to 25 ml with distilled water. The resultant solution was sprayed into the flame, and the bismuth absorption was measured. Magnesium was not added to the solutions, because the matrix elements do not interfere with the bismuth absorption, as is shown in Table 1. The results are shown in Table 5. When hydrochloric acid was added to the solution of the lead-base alloy, lead chloride precipitated on cooling; then, the supernatant solution was used for the atomic absorption measurement. The determination of bismuth after the removal of lead as chloride was successful, since little or no bismuth was lost, as has been reported by Lau *et al.*,[4] who confirmed radiometrically the recovery of over 99% of the bismuth.

In the standard addition method, the concentrations of bismuth added to the sample solutions were 0, 2, 4, 6, and 8 ppm in the final solutions. The calibration graphs for bismuth were prepared in the concentration range of 0—8 ppm.