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The Atomic Absorption Spectrophotometric Determination of Arsenic and Selenium in Premixed Inert Gas(Entrained Air)-Hydrogen Flames with a "Multi-flame" Burner

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The determination of arsenic and selenium by atomic absorption spectrophotometry was established in premixed inert gas(entrained air)-hydrogen flames using a "multi-flame" burner. Arsenic and selenium electrodeless discharge lamps were used as the sources of radiation. The optimum operating conditions for the atomic absorption measurements for arsenic and selenium at 193.7 and 196.1 nm respectively were investigated. Under the optimum conditions, the sensitivities for 1% absorption were 0.17 and 0.15 ppm for arsenic and selenium respectively. Many other elements and acids interfered with the determination of arsenic and selenium in these low-temperature flames. Most of the interferences were found to be completely eliminated, in appearance, by adding a large amount (2000 ppm) of tin(II) chloride to the sample solutions. Furthermore, a gas-sampling technique for arsenic was studied in order to improve the arsenic sensitivity and in order to eliminate the interferences from other elements. The present method was applied to the determination of arsenic in sulfide ores and steels with satisfactory results.

There are two major difficulties in the determination of arsenic and selenium by atomic absorption spectrophotometry; the first is the high flame background absorption and the noise levels obtained at the resonance lines of these elements below 200 nm, and the second is the relatively low intensity and poor stability shown by many arsenic and selenium hollow-cathode lamps. By using a hollow-cathode lamp and an air-acetylene flame, the sensitivities have been reported to be 1.0 ppm for arsenic[1-3] at 193.7 nm and to be 1.0 ppm for selenium[1-4] at 196.1 nm. Later, the present authors[5] have described the determination of selenium in sulfur and obtained the sensitivity of 0.4 ppm for 1% absorption in an air-hydrogen flame with a total-consumption nebulizer-burner.

Several attempts have been made to overcome the difficulties due to the absorptions of arsenic- and selenium-radiations by the atmosphere, by optical components, and by flame gases. Arsenic and selenium may be atomized efficiently in argon-hydrogen flame[2] and nitrogen-hydrogen flame[6] burning with entrained air. These flames exhibit greater transparencies below 200 nm than do conventional air-hydrogen or air-acetylene flames, resulting in improved signal-to-noise ratios. However, the determination of arsenic and selenium in these cool flames may suffer from interferences from various foreign elements. Kirkbright and Ranson[7] have used the slightly fuel-rich nitrous oxide-acetylene flame to remove the interferences from foregin elements. Ando *et al.*[6] have employed long-path-length Vycor cells with a nitrogen(entrained air)-hydrogen flame to determine arsenic; they thus obtained the sensitivity of 0.006 ppm for 1% absorption. Massmann[8] has used an electrically-heated graphite cell in the argon atmosphere to show the possibility of determining arsenic down to 0.1 ppm. The use of electrodeless discharge lamps as an alternative to hollow-cathode lamps in atomic absorption spectrophotometry has been reported.[3,9-13] Potentially these line sources have the advantage of having a higher output intensity and a narrower emission line free from self-absorption or self-reversal; therefore, they may allow operation at low amplifier-gain and spectral-bandpass settings.

In this investigation, the determination of arsenic and selenium in premixed inert gas (entrained air)-hydrogen flames with a "multi-flame" burner[14] has been established by using arsenic and selenium electrodeless discharge lamps as sources of radiation. The performance characteristics of the electrodeless discharge lamps, the interferences, and their elimination in the determination of both elements have been studied in detail. Furthermore, a gas-sampling technique[15] for arsenic has been studied in order to improve the sensitivity and eliminate the interferences. The present method has then been applied to the determination of arsenic in several sulfide ores and steels.

Experimental

Apparatus. A Nippon Jarrell-Ash Model AA-1 atomic absorption/flame emission spectrophotometer fitted with a HTV R—106 photomultiplier was used on a single-pass

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1) W. Slavin and S. Sprague, *At. Absorption Newslett.*, **3**, 1 (1964).

2) H. L. Kahn and J. E. Schallis, *ibid.*, **7**, 5 (1968).

3) G. F. Kirkbright, M. Sargent, and T. S. West, *ibid.*, **8**, 34 (1969).

4) C. S. Rann and A. N. Hambly, *Anal. Chim. Acta*, **32**, 346 (1965).

5) T. Nakahara, M. Munemori, and S. Musha, *ibid.*, **50**, 51 (1970).

6) A. Ando, M. Suzuki, K. Fuwa, and B. L. Vallee, *Anal. Chem.*, **41**, 1974 (1969).

7) G. F. Kirkbright and L. Ranson, *ibid.*, **43**, 1238 (1971).

8) H. Massmann, *Z. Anal. Chem.*, **225**, 203 (1967).

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10) R. M. Dagnall, K. C. Thompson, and T. S. West, *At. Absorption Newslett.*, **6**, 117 (1967).

11) R. M. Dagnall and T. S. West, *Appl. Opt.*, **7**, 1287 (1968).

12) K. E. Zacha, M. P. Bratzel, J. D. Winefordner, and J. M. Mansfield, *Anal. Chem.*, **40**, 1733 (1968).

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

15) W. Holak, *Anal. Chem.*, **41**, 1712 (1969).

system. A "multi-flame" burner[14] constructed in the authors' laboratory in conjuction with a Techtron nebulizer-chamber was also used.

The line sources employed were arsenic and selenium electrodeless discharge lamps (EMI Electronics, Ltd., Great Britain), which were operated in a 3/4-wave resonant cavity, Model 211 L, at 2450 MHz with a "Microtron 200" power generator (Electro-Medical Supplies, Ltd., Great Britain) coupled with a reflected power meter. The discharge was initiated with a "Tesla" high-frequency vacuum tester.

The hydrogen, argon and nitrogen flow rates were controlled by means of needle valves and were measured on calibrated flow meters.

Reagents. A standard arsenic solution (1000 ppm) was prepared by dissolving 1.386 g of arsenious oxide of an analytical-reagent grade with 2 g of sodium hydroxide and 20 ml of distilled water, by neutralizing with hydrochloric acid, and by then diluting the solution to 1000 ml with distilled water.

A stardard selenium solution (1000 ppm) was prepared by dissolving 1.000 g of high-purity selenium metal in 5 ml of nitric acid and by then diluting the solution to 1000 ml with distilled water.

Diluted solutions of arsenic and selenium were prepared from the stock solutions as required.

All the acids and inorganic salts used were of either an analytical-reagent grade or the highest quality available.

Results and Discussion

Wavelengths and Flame Conditions. The relative intensities and sensitivities of the arsenic and selenium lines radiated from the electrodeless discharge lamps indicated that the arsenic 189.0-nm line was the most sensitive, but when we take the noise levels into consideration the arsenic 193.7-nm line was the most useful, while the selenium 196.1-nm line was the most sensitive and useful.

The effect of the flame composition and the flame height on the arsenic and selenium atomic absorptions was studied in premixed inert gas(entrained air)-hydrogen flames. The flame composition and the flame height had remarkable effects on the arsenic and selenium atomic absorptions in these flames. The optimum flame conditions obtained for arsenic and selenium are shown in Table 1.

TABLE 1. OPTIMUM FLAME CONDITIONS FOR ARSENIC AND SELENIUM

	Arsenic	Selenium
Argon (entrained air)-hydrogen flame		
Hydrogen flow rate (l/min)	9.4	7.2
Argon flow rate (l/min)	4.5	4.5
Argon pressure (kg/cm^2)	1.5	1.5
Sample aspiration rate (ml/min)	8.9	8.9
Flame height above burner head (mm)	4.0	2.0
Nitrogen (entrained air)-hydrogen flame		
Hydrogen flow rate (l/min)	9.4	6.5
Nitrogen flow rate (l/min)	5.0	5.0
Nitrogen pressure (kg/cm^2)	1.5	1.5
Sample aspiration rate (ml/min)	9.0	9.0
Flame height above burner head (mm)	5.0	3.0

Optimization of Some Experimental Parameters in the Operation of Microwave-excited Electrodeless Discharge Lamps. Many workers have used microwave-excited electrodeless discharge lamps in atomic absorption and atomic fluorescence spectrophotometry, and have described their advantages and limitations.[11-13,16-18] Since the performance characteristics of the electrodeless discharge lamps are not always identical, it appeared necessary to establish the optimum operating conditions of each electrodeless discharge lamp employed. The efficiency with which the electrodeless discharge lamps were operated was found to depend to a large extent on the proper choice of resonant cavity. The electrodeless discharge lamps employed in this study were not discharged in a 3/4-wave resonant cavity Model 210 L (Electro-Medical Supplies, Ltd.) under any circumstance.

Although it had been expected[19] that tuning was dependent on the discharge characteristics and, consequently, dependent upon the microwave power applied, a change in the tuning characteristics with a variation in the microwave power is generally impossible to detect. Consequently, apart from occasional checks, the cavity was tuned to give as low a reflected power as possible. A reflected-power meter may be used to facilitate the tuning of the cavity and to ensure that the reflected power is not so high that the mag-

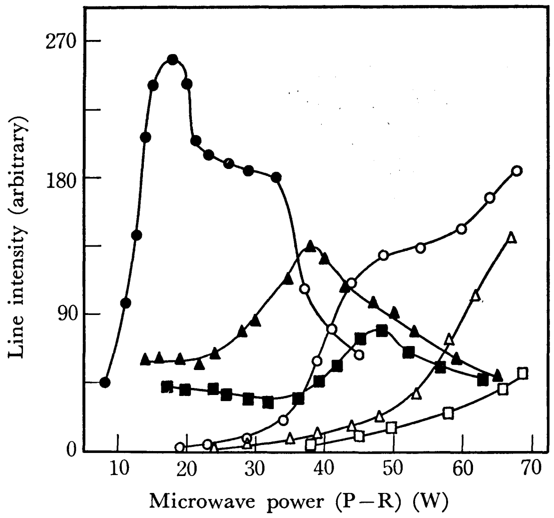

Fig. 1. Effect of microwave power on line intensities of arsenic and selenium.
At the 193.7 nm arsenic line
—●— Without cooling
—▲— With cooling (nitrogen flow rate : 2 l/min)
—■— With cooling (nitrogen flow rate : 3 l/min)
At the 196.1 nm selenium line
—○— Without cooling
—△— With cooling (nitrogen flow rate : 3 l/min)
—□— With cooling (nitrogen flow rate : 6 l/min)

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16) J. M. Mansfield, M. P. Bratzel, H. O. Norgordon, K. E. Zacha, D. O. Knapp, and J. D. Winefordner, *Spectrochim. Acta*, **23B**, 389 (1968).

17) C. H. Corliss, W. R. Borzmann, and F. O. Westfall, *J. Opt. Soc. Amer.*, **43**, 398 (1953).

18) D. C. Cooke, R. M. Dagnall, and T. S. West, *Anal. Chim. Acta*, **54**, 381 (1971).

19) F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, *Rev. Sci. Instr.*, **36**, 294 (1965).

netron may be damaged. Provided that powers not higher than about 75 W are used, there is little possibility of damage being caused, and visual tuning to maximum lamp intensity is quite satisfactory.

The effect of microwave power (the power indicated on the microwave generator minus the reflected power (P–R) was taken) on the resonance-line intensity was examined for arsenic and selenium electrodeless discharge lamps. The results obtained are shown in Fig. 1. The cooling of electrodeless discharge lamps has been recommended by some workers.[20,21] As is shown in Fig. 1, a decrease in the line intensity was observed with both electrodeless discharge lamps when they were cooled with nitrogen. Furthermore, the maximum in the intensity of the 193.7-nm arsenic line shifted from a lower to a higher microwave power with an increase in the nitrogen flow rate. Although the line intensities were decreased with an increase in the nitrogen flow rate, the cooling produced an increased stability and considerably shorter warming-up periods by means of improved insulation from draughts. However, it was necessary for the flow rate of cooling nitrogen to be accurately regulated; otherwise, the cooling rather resulted in poor stability. In this study, the nitrogen from a cylinder was used as the cooling gas after drying with anhydrous calcium chloride instead of dry air, because a small pressure variation in an air compressor remarkably affected the line intensity with both elelectrodeless discharge lamps employed.

Then, the effect of the microwave power (P–R) on the atomic absorption signals of arsenic and selenium was examined. The absorbance variations obtained in the microwave power range from 8 to 70 W with and without the use of nitrogen cooling are shown in Fig. 2. The arsenic atomic absorption was remarkably increased with a decrease in the microwave power, while no or little variation with microwave power was observed for selenium. As is shown in Fig. 2, the nitrogen cooling produced an increase in the atomic absorption signals. However, a nitrogen flow rate of more than 2.0 l/min gave a constant absorbance for either arsenic or selenium. This phenomenon is presumably due to the fact that there is little or no self-absorption and/or self-reversal effects so long as the microwave power is small. Particularly for arsenic, this may be the case. A self-reversal effect has been noticed with some microwave-excited electrodeless discharge lamps,[22] but this may be readily overcome by using a slightly reduced operating microwave power and/or by cooling the lamp, as has been described above.

Thus, the optimization of the microwave power and the nitrogen cooling was important to the atomic absorption signal rather than the line intensity. The short-term stability of the lamps employed was similar, virtually better than 5% and often 2%, and the drift rate was less than 2% per hour for both arsenic and selenium lamps.

The optimum operating conditions for the atomic absorptions of arsenic and selenium may be summarized as follows. The microwave power(P–R) values were 8 and 20 W for arsenic and selenium respectively. The flow rate of nitrogen as a cooling gas was 2.0 l/min; it was accurately controlled with a needle valve and measured on a calibrated flow meter.

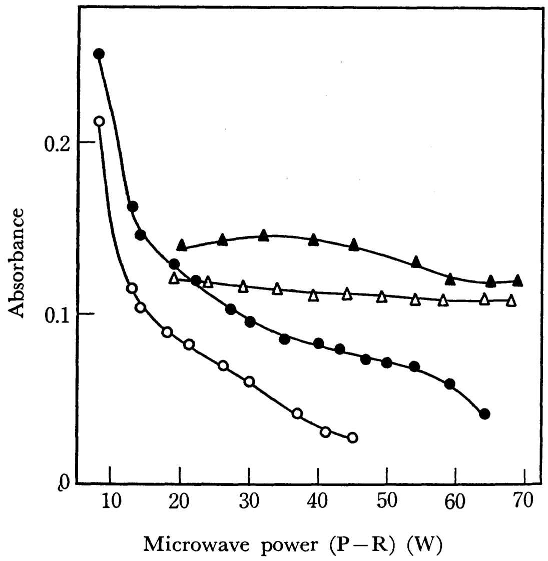

Fig. 2. Effect of microwave power on the determination of arsenic and selenium.
At the 193.7 nm arsenic line
—●— With cooling, —○— Without cooling
At the 196.1 nm selenium line
—▲— With cooling, —△— Without cooling

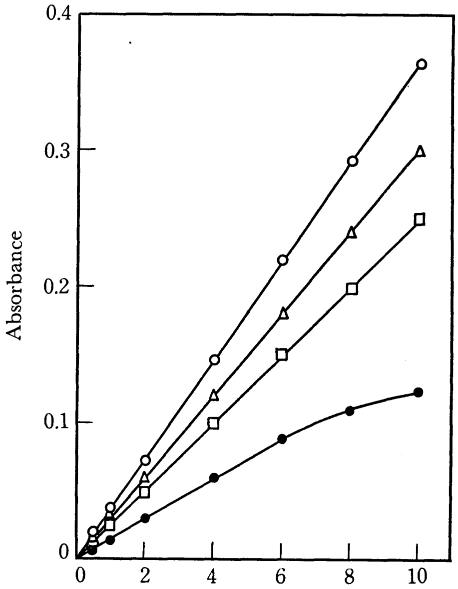

Fig. 3. Calibration graphs for arsenic and selenium in argon (entrained air)-hydrogen flame.
—○— At 189.0 nm arsenic line (microwave power : 8 W)
—△— At 196.1 nm selenium line (microwave power : 20 W)
—□— At 193.7 nm arsenic line (microwave power : 8 W)
—●— At 193.7 nm arsenic line (microwave power : 19 W)

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[20] R. F. Browner, R. M. Dagnall, and T. S. West, *Anal. Chim. Acta*, **46**, 207 (1969).

[21] R. M. Dagnall, G. F. Kirkbright, and T. S. West, *ibid.*, **47**, 407 (1969).

[22] R. M. Dagnall, K. C. Thompson, and T. S. West, *Talanta*, **14**, 1151 (1967).

Calibration Graphs for Arsenic and Selenium. The calibration graphs for arsenic and selenium in the argon(entrained air)-hydrogen flame under the optimum experimental conditions described above were linear in the range of 0—10 ppm, as is shown in Fig. 3, with a precision of the mean relative standard deviation of about 3%, but the graph obtained at the 193.7-nm arsenic line with the higher microwave power (19 W) was bent slightly towards the concentration axis from 6 to 10 ppm. This bending is presumably due to self-absorption and/or self-reversal effects at a higher microwave power. The sensitivities (ppm for 1% absorption) over the linear ranges were found to be 0.17 and 0.15 ppm at the 193.7-nm arsenic line and the 196.1-nm selenium line respectively. No appreciable difference in the sensitivities between the argon(entrained air)-hydrogen flame and the nitrogen (entrained air)-hydrogen flame was observed.

Effects of Acids on the Atomic Absorptions of Arsenic and Selenium. The effects of the acids generally used for the dissolution of various practical samples in the determination of arsenic and selenium were examined in both the flames. The acids were hydrochloric, nitric, perchloric, phosphoric, and sulfuric acids. The concentrations of arsenic and selenium were 10 and 15 ppm respectively, and the concentration range of the acids was 0–3.0 N. The results obtained for arsenic in the argon(entrained air)-hydrogen flame are shown in Fig. 4. Similar results for selenium were obtained in both the flames. Hydrochloric, nitric, and perchloric acids had little effect on the atomic absorptions of arsenic and selenium, while sulfuric acid caused either an enhancement or depression, depending on its concentration. Phosphoric acid caused a depressing interference, independent of its concentration. The present authors have reported previously that hydrochloric, nitric, perchloric, and phosphoric acids, unlike sulfuric acid, had no effect on the selenium atomic absorption at the 196.1-nm line in the hotter air-hydrogen flame with a total-consumption nebulizer-burner.[5)]

It was noted that the solutions containing nitric, perchloric, phosphoric, and sulfuric acids in the absence of both arsenic and selenium gave background absorptions at 193.7 and 196.1 nm in the inert gas(entrained air)-hydrogen flames under the optimum contions for the arsenic and selenium atomic absorptions. These background absorptions were not linear with respect to their concentrations. The background absorbances at 193.7 nm were found to be 0.101, 0.053, 0.026, and 0.019 in the argon(entrained air)-hydrogen flame for sulfuric, phosphoric, perchloric, and nitric acids respectively at a 3.0-N concentration level, and to be 0.107, 0.050, 0.021, and 0.011 in the nitrogen (entrained air)-hydrogen flame for sulfuric, phosphoric, nitric, and perchloric acids respectively at the same concentration level. The results shown in Fig. 4 have been corrected for the background absorptions at each concentration of the acids. The background absorption seems to be ascribable to the molecular absorption, the light scattering, and/or the variation in the refractive index within the flame caused by vaporization of concentrated solutions.[5)]

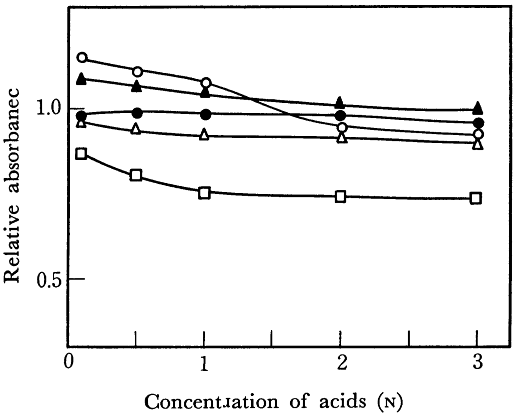

Fig. 4. Effect of acids on the determination of arsenic in argon (entrained air)-hydrogen flame.
Concentration of arsenic : 10 ppm
—○— Sulfuric acid, —▲— Perchloric acid,
—●— Hydrochloric acid, —△— Nitric acid,
—□— Phosphoric acid

Effects of Foreign Elements on the Determination of Arsenic and Selenium. The effects of various foreign elements on the determination of arsenic and selenium have been studied in an air-hydrogen,[5)] an air-acetylene flame,[23)] and a nitrogen-shielded air-acetylene flame.[3)] The present authors have established that the determination of tin[24)] and bismuth[25)] in premixed inert gas(entrained air)-hydrogen flames suffer from interference from foreign elements because of the inability of the cool flames to vaporize or atomize the other elements present in the sample solutions. The interference effects of various other elements on the atomic absorptions of arsenic and selenium were studied in inert gas(entrained air)-hydrogen flames under the optimum conditions established above. The atomic absorptions were recorded in the presence of a 20-fold weight excess of diverse elements for 10 and 5 ppm of arsenic and selenium respectively. The results obtained in the argon(entrained air)-hydrogen flame are shown in Table 2. It can be seen from Table 2 that many elements produce depressing interferences with the determination of arsenic and selenium. The depressing interferences due to antimony, cadmium, manganese, selenium, and bismuth in the determination of arsenic, and those due to barium, lead, mercury, and zinc in the determination of selenium, were completely overcome by using a slightly acidic solution (0.2–0.5 N in hydrochloric acid). These interferences may also be overcome by using a hotter flame, such as a nitrous oxide-acetylene flame.[7)]

However, further investigations of the depressing interferences indicated that most of the depressing interferences with the arsenic and selenium atomic absorptions were eliminated, in appearance, by adding a great amount (2000 ppm) of tin to the sample solutions, as is shown in Table 3. Although the

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23) C. L. Chakrabarti, *Anal. Chim. Acta*, **42**, 379 (1968).

24) T. Nakahara, M. Munemori, and S. Musha, *ibid.*, **62**, 267 (1972).

25) T. Nakahara, M. Munemori, and S. Musha, This Bulletin, **46**, 1166 (1973).

TABLE 2. EFFECT OF VARIOUS OTHER ELEMENTS ON THE DETERMINATION OF ARSENIC AND SELENIUM

Element[g]	Relative absorbance		Element[g]	Relative absorbance	
	Arsenic[h]	Selenium[i]		Arsenic[h]	Selenium[i]
None	1.00	1.00	Mn[a]	0.82	0.33
Ag[a]	0.98	1.04	Mo[f]	0.86	0.84
Al[b]	0.92	0.25	Na[b]	1.00	1.01
As[c]	—	0.96	Ni[e]	0.29	0.64
Au[b]	1.00	0.89	Pb[a]	0.98	0.42
B[d]	0.85	1.04	Pd[b]	0.35	0.32
Ba[b]	1.00	0.54	Pt[b]	0.98	0.90
Be[e]	0.85	0.91	Rb[b]	1.02	1.00
Bi[a]	0.97	0.99	Sb[b]	1.01	1.00
Ca[a]	0.94	0.74	Se[c]	0.92	—
Ce[e]	0.94	0.74	Si[c]	0.22	0.21
Co[b]	0.76	0.72	Sn[b]	1.06	1.07
Cr[b]	0.79	0.53	Sr[a]	0.85	0.67
Cs[b]	1.03	0.99	Te[c]	1.05	1.03
Cu[e]	1.05	0.92	Th[a]	0.53	0.31
Fe[b]	0.88	0.92	Ti[b]	1.05	0.96
Hg[b]	0.89	0.87	Tl[a]	0.99	1.00
In[b]	1.01	0.98	V[f]	1.02	1.03
K[b]	1.01	1.00	W[c]	1.03	1.02
La[b]	0.93	0.81	Y[a]	0.37	0.00
Li[b]	1.04	0.89	Zn[a]	0.86	0.97
Mg[b]	0.99	0.88	Zr[a]	0.80	0.53

a) Added as nitrate. b) Added as chloride. c) Added as sodium arsenite, selenite, silicate, tellurite or tungstate, respectively. d) Added as boric acid. e) Added as sulfate. f) Added as ammonium molybdate or vanadate, respectively. g) The concentration of the elements added, 200 ppm for arsenic and 100 ppm for selenium. h) The concentration of arsenic was 10 ppm. i) The concentration of selenium was 5 ppm.

TABLE 3. EFFECT OF TIN ON THE DEPRESSING INTERFERENCES WITH THE DETERMINATION OF ARSENIC IN AN ARGON (ENTRAINED AIR)-HYDROGEN FLAME

Element[a]	Relative absorbance for arsenic[b]				
	Tin added (ppm)				
	0	2000	5000	10000	2000
Al	0.84	1.04	1.03	1.05	1.00
B	0.80	1.00	1.00	1.06	1.05
Ca	0.86	1.03	0.98	0.97	0.98
Co	0.88	0.93	0.95	0.94	0.95
Cr	0.87	0.99	1.00	1.03	1.06
Fe	0.79	1.05	1.04	1.03	1.05
Mo	0.78	0.99	0.98	1.01	1.00
Ni	0.48	1.02	0.99	0.98	1.03
Si	0.67	0.95	0.96	0.94	0.95
V	0.88	1.01	0.99	0.99	1.00
Zr	0.73	0.96	0.98	0.98	0.95

a) The concentration of the elements added was 1200 ppm.
b) The concentration of arsenic was 10 ppm.

mechanism of the elimination of the depressing interferences in the presence of tin has not been explained satisfactorily, the present method could be applied to the determination of arsenic or selenium in some practical samples with satisfactory results.

Gas-sampling Technique for the Determination of Arsenic. Arsenic often needs to be determined in trace amounts, and an improvement in the sensitivity of the atomic absorption spectrophotometric method would be desirable. This can be achieved if arsenic is generated from the sample solution, col-

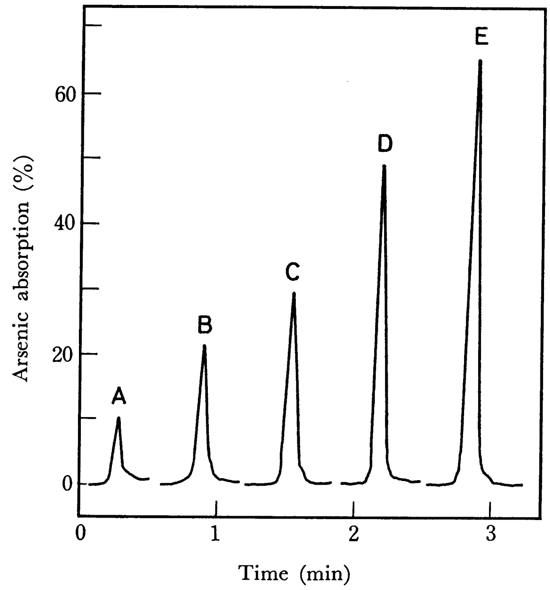

Fig. 5. Arsenic atomic absorption signals by gas-sampling technique.
Flame: Argon (entrained air)-hydrogen flame
A: Reagent blank B: 0.05 μg of arsenic
C: 0.1 μg of arsenic D: 0.2 μg of arsenic
E: 0.4 μg of arsenic

lected in a cold trap with, for example, liquid nitrogen, and then passed into the burner of an atomic absorption spectrophotometer; the atomic absorption signal is recorded as a function of the time. Holak[15] has reported this gas-sampling technique for arsenic determination by atomic absorption spectrophotometry, and obtained the detection limit of 0.04 μg of arsenic.

This gas-sampling technique was applied to the present method. Examples of response signals are shown in Fig. 5. A preliminary study indicated that the sensitivity for 1% absorption was 0.004 μg (4 ng) in quantities or 0.13 ppb in concentration, and Beer's law was established as holding between the absorbance and the amount of arsenic.

The main advantage of the gas-sampling technique is its suitability for trace analysis. The element is isolated from the matrix elements, and the total quantity is used to produce a sharp absorption signal. In addition, interferences often associated with solutions, such as those with high concentrations, and light scattering, as well as chemical interferences, are virtually eliminated.

Determination of Arsenic in Sulfide Ores and Steels. Based on the above-mentioned observations, the following procedures for the determination of arsenic in sulfide ores and steels were developed.

A 0.5-g ore sample was weighed and dissolved in 25 ml of diluted *aqua regia* by gentle heating on a hot plate. After the solution had then been cooled, the insoluble solids (sulfur and silicate) were filtered off with a filter paper. The filtrate was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. Determinations were made by the standard addition method, and also by the calibration graph method. In either case the arsenic atomic absorptions were measured at 193.7 nm in the presence of 2000-ppm tin (as stannous chloride) as a suppressor of the interferences from other elements under the above-mentioned optimum operating conditions. The results of the determination of arsenic in sulfide ores by atomic absorption spectrophotometry are shown in Table 4.

TABLE 4. RESULTS OF THE DETERMINATION OF ARSENIC IN SULFIDE ORES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Sample	Arsenic content (%)			
	Ar–H$_2$ a)		N$_2$–H$_2$ b)	
A mine ore (Cu conc.)	0.29_2 c)	0.28_4 d)	0.28_3 c)	0.29_1 d)
	0.31_7 c)	0.28_9 d)	0.29_2 c)	0.28_3 d)
	0.27_9 c)	0.29_3 d)	0.28_2 c)	0.29_5 d)
B mine ore (S conc.)	0.45_1 c)	0.44_5 d)	0.45_9 c)	0.45_2 d)
	0.46_3 c)	0.44_9 d)	0.44_8 c)	0.45_6 d)
	0.45_5 c)	0.46_1 d)	0.45_0 c)	0.45_4 d)

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

TABLE 5. RESULTS OF THE DETERMINATION OF ARSENIC BY ATOMIC ABSORPTION SPECTROPHOTOMETRY IN CONJUNCTION WITH A GAS-SAMPLING TECHNIQUE

Sample	Arsenic content (%)	
	Cert. value	Atomic absorption method
GK–9 Stainless steel a)	0.012	0.011_8 b)
GK–10 Cast iron a)	0.029	0.028_5 b)

a) Supplied by Kansai Bunseki Kenkyukai.
b) An average of 5 determinations.

A 0.1-g steel sample was weighed and dissolved in 10 ml of *aqua regia* by heating on a hot plate. After evaporation to dryness, the residue was dissolved in 10 ml of hydrochloric acid by gentle heating on a hot plate. The solution was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. The resultant solution was employed as the sample solution. The determination of arsenic was followed below. A 5-ml portion of the sample solution was transferred into a 300-ml Erlenmeyer flask, and 0.5 ml of a 35% stannous chloride solution, 40 ml of 6 N hydrochloric acid, and 5 ml of a 20% potassium iodide solution were added. After about 10 min, 5 g of sandy zinc metal were added and the arsine generated was collected with a U-tube filled with glass beads in liquid nitrogen. The U-tube was removed from the liquid nitrogen and allowed to come to room temperature. The arsenic atomic absorption signals were measured at 193.7 nm in the argon(entrained air)-hydrogen flame. The results are shown in Table 5.

We would like to thank the Ministry of Education for its Scientific Research Grant to one of us (M. M.).