Nondispersive and Dispersive Atomic Fluorescence Spectrometry of Arsenic by Utilizing the Arsine-generation Technique

Taketoshi Nakahara,* Toshiaki Tanaka, and Sôichirô Musha
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Mozu-umemachi, Sakai 591

(Received January 5, 1978)

Atomic fluorescence spectrometry with nondispersive and dispersive systems by utilizing the arsine-generation technique is described for the determination of arsenic at the nanogram level, where the premixed argon (entrained air)– and nitrogen(entrained air)–hydrogen flames and a microwave-excited electrodeless discharge lamp were used. For the low-temperature flames, a newly designed burner has been constructed. The best detection limits obtained for arsenic are 2.3 ng in mass and 0.12 ppb in concentration with a nondispersive system in argon(entrained air)–hydrogen flame. Linear analytical working curves covering the mass range of arsenic from 30 ng to around 1000 ng have been obtained with nondispersive and dispersive systems at 193.7 and 197.2 nm in both the hydrogen flames. Several elements including other hydride-forming elements, such as antimony, bismuth, selenium, and tellurium, have caused a decrease in fluorescence signals. The present method, with the most sensitive nondispersive system and argon(entrained air)–hydrogen flame, can be applied to the determination of trace amounts of arsenic in wastewaters.

In atomic fluorescence spectrometry by the direct nebulization of solutions into flame, some authors[1–6] have reported detection limits of 0.2—25 ppm of arsenic with a dispersive system, mostly at 189.0, 193.7, 197.2, and 235.0 nm, while others[7–9] have obtained the detection limits of 0.3—6 ppm of arsenic with a nondispersive system. For both systems they have used an arsenic electrodeless discharge lamp as the radiation source and air–acetylene, oxygen–, argon(entrained air)–, and nitrogen(entrained air)–hydrogen flames as the atom reservoir. Dagnall *et al.*[10] have applied the atomic fluorescence method to the determination of arsenic in nickel-base alloys and obtained a detection limit of 1.4 ppm of arsenic at 193.7 nm with a nitrogen (entrained air)–hydrogen flame and an arsenic electrodeless discharge lamp.

On the other hand, in atomic absorption spectrometry the sensitivity for arsenic has been remarkably improved by using an arsine-generation technique based on the reduction of arsenic to arsine and the introduction of the generated arsine into an atom reservoir (flame, heated quartz tube, or heated graphite furnace). As the reductant, zinc,[11–17] sodium tetrahydroborate,[17–24] and titanium trichloride and magnesium rod[25] have been used. Especially for arsenic, zinc has been recommended as a reductant.[15,17]

Tsujii and Kuga[26] have reported a detection limit of 2 ng of arsenic by nondispersive atomic fluorescence spectrometry with an arsine-generation technique in which arsenic is reduced by zinc to arsine. Thompson[27] has described a dispersive atomic fluorescence method at 193.7 nm in conjunction with an arsine-generation technique using sodium tetrahydroborate as a reductant; by using this method he obtained a detection limit of 0.1 ng of arsenic for a sample volume of 1.0 ml.

Recently the present authors have designed and constructed an atomic fluorescence spectrometer which can be used with both dispersive and nondispersive systems. They have demonstrated the performance of the newly constructed spectrometer by measuring mercury atomic fluorescence signals with dispersive and nondispersive systems combined with the cold-vapor technique.[28] This paper will describe the nondispersive and dispersive atomic fluorescence spectrometric determination of arsenic by using the arsine-generation technique and the premixed argon(entrained air)– and nitrogen-(entrained air)–hydrogen flames produced with a new burner constructed in this laboratory. The interference effects of acids and diverse elements on the fluorescence signals of arsenic were examined. The most sensitive nondispersive atomic fluorescence method was also applied to the determination of arsenic in wastewater samples with satisfactory results.

Experimental

Reagents. All the reagents used were of an analytical reagent grade. The stock solution of arsenic, 1000 ppm, was prepared by dissolving 1.320 g of diarsenic trioxide in 20 ml of 2.5 mol dm^{-3} sodium hydroxide and by diluting to 1000 ml with a 5% sulfuric acid–20% hydrochloric acid solution. The diluent for the stock solution was a 5% sulfuric acid–20% hydrochloric acid solution. Diluted arsenic standard solutions were prepared immediately before use by dilution of the stock solution with the diluent.

Also used were: tin(II) chloride (10% $SnCl_2 \cdot 2H_2O$ in 6 mol dm^{-3} hydrochloric acid), potassium iodide (20% in distilled water), and zinc tablets. Zinc tablets were prepared as has previously been described.[17] Each tablet was 10 mm in diameter, 3 mm thick, and approximately 0.6 g in weight.

Apparatus. All the measurements were made with a laboratory-constructed atomic fluorescence spectrometer,[28] equipped with a Nippon Jarrell-Ash Model ASD-1A arsenic measurement unit and a newly constructed burner (*vide infra*). The atomic fluorescence instrument used contained the specific components shown in Table 1.

Burner. The present authors have reported the performance of a "multi-flame" burner of the slot type for atomic absorption spectrometry.[29] Based on a similar concept for premixed hydrogen flames, we designed and constructed a nitrogen-sheathed, water-cooled burner which can produce premixed argon (entrained air)– and nitrogen(entrained air)–hydrogen flames for atomic fluorescence measurements; the burner is shown in Fig. 1. It consists of a burner top and its holder, both of which are made of brass. To ensure the adequate entrainment of secondary air, the outer surface of the nozzle is tapered. Inside the burner is placed a porous ceramic plate which contains about 50 holes(0.5 mm in diameter) per cm^2 and is 1.25 cm thick, to maintain the stability of the hydrogen flames of a higher burning velocity. In this study the new burner was fitted to a Techtron nebulizer chamber. A schematic diagram of the apparatus used in this work is shown in Fig. 2. The right half of the figure represents a nondispersive atomic fluorescence spectrometer. For a dispersive measuring system, the photomultiplier and its housing (10 in Fig. 2) are replaced by a monochromator equipped with a photomultiplier. The fluorescence radiation is measured at right angles to the axis of the optical path from the light source to the flame.

Procedures. The optimum instrumental variable settings used for the atomic fluorescence measurements are shown in Table 2. The arsine generated by the procedure previously reported for the atomic absorption spectrometry of arsenic[17)] was introduced into premixed argon(entrained air)- and nitrogen(entrained air)-hydrogen flames in which argon and nitrogen respectively were used as the carrier gas as well as the auxiliary gas. The fluorescence signal was recorded on the pen recorder for the peak-height measurement throughout this work.

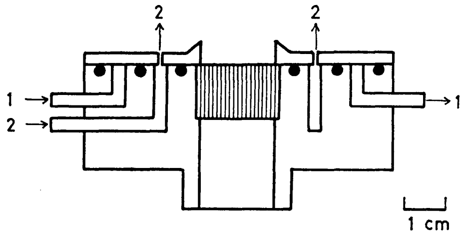

Fig. 1. Cross-sectional diagram of nitrogen-sheathed, water-cooled burner for atomic fluorescence measurements with premixed argon (entrained air)- and nitrogen (entrained air)-hydrogen flames.
1: Cooling water, 2: sheath gas, ▥: ceramic plate, ●: O-rings.

Table 1. Experimental components of the atomic fluorescence instrument used in this study

Item	Description (model No.) and supplier
Power stabilizer	A-133, NF Circuit Design Block
Light source and power	
Lamp	As electrodeless discharge lamp, EMI
Power supply	Microtron 200, Electro-Medical Supplies
Resonant cavity	Model 211 L, Electro-Medical Supplies
Light chopper	Laboratory-made
Lens	30-mm diameter, 75-mm focal length, quartz
Burner	Laboratory-made
Monochromator	JE-30, Nippon Jarrell-Ash
Photomultiplier	R-166 ("solar-blind" type, for nondispersive system) and R-106 UH (for dispersive system), Hamamatsu TV
High-voltage power supply for photomultiplier	412 B, John-Fluke
Preamplifier	JP 406, Nippon Jarrell-Ash
Operational amplifier	2F/4539B, Akikoh Electric
Power supply	±15 V, Laboratory-made
Lock-in amplifier	572B, NF Circuit Design Block
Oscilloscope	CS-1351, Trio
Recorder	QPD$_{54}$, Hitachi
Arsine-generating unit	ASD-1A, Nippon Jarrell-Ash

Results and Discussion

Atomic Fluorescence Spectrum of Arsenic. The spectral characteristics of all 15 lines of arsenic have been found by the solution-nebulization technique to exhibit atomic fluorescence in air–acetylene and argon– and nitrogen–hydrogen flames.[1)] With the dispersive system, the spectral characteristics of the emission and fluorescence of all 15 lines of arsenic were examined in this study. The results obtained are shown in Table 3. With the present instrument, the 193.7 nm line gave the highest sensitivity in both the hydrogen flames. The values shown in Table 3 were not corrected for the photomultiplier spectral response.

Effect of Microwave Power. The present authors have previously described the relationship between the emission intensity of the arsenic 193.7 nm line and the microwave power applied for an arsenic electrodeless discharge lamp used for atomic absorption spectrometry.[30)] In atomic fluorescence spectrometry for arsenic with the same arsenic electrodeless discharge lamp, the effect of microwave power ranging 18 to 40 W on the fluorescence signals was examined with the dispersive system at 193.7 nm. The results obtained were analogous to those previously reported in atomic absorption spectrometry.[30)] This phenomenon can be easily explained on the base of the theoretical concept that the atomic fluorescence energy is directly proportional to the spectral irradiance of the light source.[31–33)] The optimum power used is shown in Table 2.

Effect of Flame Composition and Flame Height. Tsujii and Kuga[26)] have reported that the flame composition was not a critical factor with regard to the fluorescence

Table 2. Optimum experimental conditions

Microwave power applied	24 W (Incident power, 35 W; Reflected power, 11 W)
RC time constant	1.0 s
High voltage for photomultiplier	700 V
Load resistance	470 kΩ
Modulation frequency	90 Hz (for nondispersive system) and 240 Hz (for dispersive system)
Volume of sample	20 ml
Zinc tablet	One piece (Zn 0.6 g)
Potassium iodide solution	1.0 ml
Tin(II) chloride solution	1.0 ml
Hydrogen flow rate	3.6 l min^{-1}
Argon or nitrogen flow rates	Carrier 4.0 l min^{-1} Auxiliary 2.0 l min^{-1}
Nitrogen flow rate for flame sheathing	1.0 l min^{-1}
Flame height	4 cm (for argon (entrained air)-hydrogen flame) and 5 cm (for nitrogen (entrained air)-hydrogen flame)

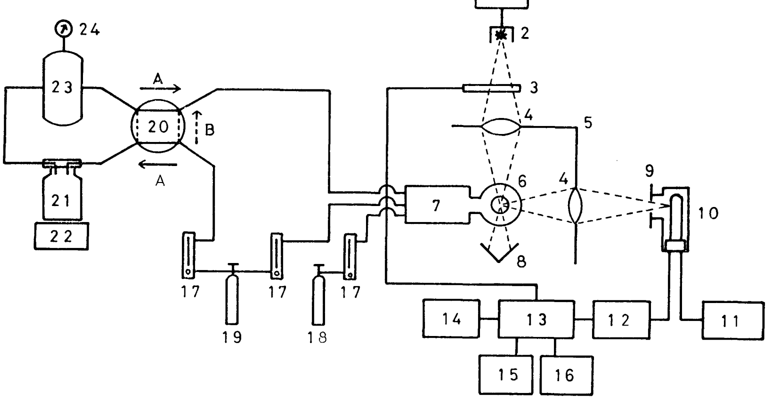

Fig. 2. Schematic diagram of the nondispersive atomic fluorescence instrument employed in this work.
1: Microwave generator, 2: electrodeless discharge lamp and resonant cavity, 3: light chopper, 4: lenses, 5: panel, 6: burner, 7: nebulizer chamber, 8: light trap, 9: diaphragm, 10: photomultiplier and its housing, 11: high-voltage power supply, 12: preamplifier, 13: lock-in amplifier, 14: line-power stabilizer, 15: oscilloscope, 16: pen recorder, 17: flowmeters, 18: hydrogen cylinder, 19: argon or nitrogen cylinder, 20: four-way stopcock, 21: reaction flask, 22: magnetic stirrer, 23: collection vessel, 24: pressure gauge, A: "sweep" gas flow, B: "by-pass" gas flow.

TABLE 3. ATOMIC FLORESCENCE SPECTRUM OF ARSENIC

Wavelength (nm)	Emission intensity of As electrodeless discharge lamp[a]	Fluorescence signal[b] Ar(air)-H_2[c]	Fluorescence signal[b] N_2(air)-H_2[d]
189.0[e]	7.9	13.0	5.6
193.7[e]	14.0	22.0	6.2
197.2[e]	14.7	18.0	5.0
228.8[f]	48.0	0.5	0.2
235.0[f]	54.0	0.8	1.5
238.1[g]	88.5	1.5	1.3
243.7[g]	20.5	1.0	0.6
245.7[g]	80.0	2.6	3.1
249.3[g]	62.5	4.2	5.0
274.5[f]	8.5	N. D.[h]	N. D.[h]
278.0[f]	25.0	1.2	0.8
286.0[f]	17.2	1.0	0.7
289.9[f]	3.8	N. D.[h]	N. D.[h]
303.3[g]	13.0	1.5	1.0
312.0[g]	5.2	N. D.[h]	N. D.[h]

a) Scale reading for each line from the lamp discharged at 24 W. b) Scale reading for 100-ng arsenic at the same measuring conditions. c) Argon (entrained air)-hydrogen flame. d) Nitrogen (entrained air)-hydrogen flame. e) Resonance fluorescence. f) Thermally-assisted direct-line fluorescence. g) Direct-line fluorescence. h) Not detected.

intensity, but that the noise level remarkably affected by the flame composition in the argon(entrained air)-hydrogen flame.

In argon(entrained air)- and nitrogen(entrained air)-hydrogen flames, the effects of the flame composition and the flame height on the fluorescence signals of arsenic were examined over the range of hydrogen flow rate of 1.8—4.5 l min^{-1}, with the flow rate of argon or nitrogen kept constant. The results obtained in the argon(entrained air)-hydrogen flame with the nondispersive system are shown in Fig. 3. Similar results were obtained in the nitrogen(entrained air)-hydrogen flame. As is shown in Fig. 3, the fluorescence signals varied remarkably with the variations in the flame composition and the flame height above the burner top. Taking account of noise levels, the optimum conditions for the flames were determined to be as is shown in Table 2. The flow rate of nitrogen as a sheath gas was fixed at 1.0 l min^{-1} throughout this work, because the flow rate did not affect the fluorescence signals in the range of 1.0 to 5.0 l min^{-1}.

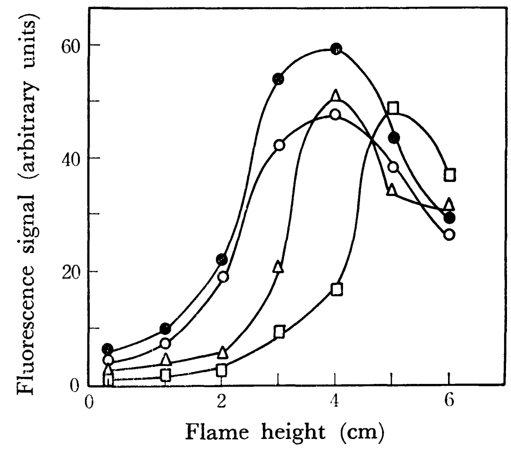

Fig. 3. Effect of flame composition and flame height on the fluorescence measurements.
Flame: argon (entrained air)-hydrogen flame, arsenic: 400 ng, argon flow rate for carrier gas: 4.0 l min^{-1}, argon flow rate for auxiliary gas: 2.0 l min^{-1}, hydrogen flow rates: ○ 1.8 l min^{-1}, ● 2.7 l min^{-1}, △ 3.6 l min^{-1}, □ 4.5 l min^{-1}.

Effect of Flow Rate of Carrier Gas. The fluorescence signals with the nondispersive system increased

TABLE 4. EFFECT OF VARIOUS OTHER ELEMENTS

Element[a]	Relative fluorescence signal[b]	Reaction time for 30 kPa (s)
None	1.00	90
B[c]	1.15	90
V[d]	1.07	75
Rb[e]	1.07	100
W[f]	1.07	75
In[e]	1.04	120
K[e]	1.02	90
Cu[g]	1.02	35
Au[e]	1.01	60
Si[f]	1.01	75
Y[g]	0.99	115
Mn[e]	0.98	120
Mg[e]	0.97	90
Cs[e]	0.94	80
Na[e]	0.94	95
Zn[e]	0.93	75
Ag[g]	0.90	40
Co[e]	0.89	20
Be[h]	0.89	80
Fe[e]	0.88	60
Ni[e]	0.88	20
Tl[g]	0.87	120
Zr[e]	0.86	65
Cd[e]	0.85	90
Bi[g]	0.84	300
La[e]	0.81	100
Ca[e]	0.81	90
Al[e]	0.80	80
Cr[e]	0.78	60
Se[f]	0.76	40
Li[e]	0.72	80
Ba[e]	0.71	60
Sb[e]	0.51	10
Mo[d]	0.47	90
Hg[e]	0.44	165
Te[e]	0.41	20
Pt[e]	0.07	10
Pd[e]	0.05	20

a) The amount added, 400 μg. b) Relative to atomic fluorescence signal for 400-ng arsenic. c) Added as boric acid. d) Added as ammonium vanadate or molybdate respectively. e) Added as chloride. f) Added as sodium tungstate, silicate, or selenite respectively. g) Added as nitrate. h) Added as sulfate.

with an increase in the flow rates of the carrier gas up to 4.0 l min^{-1} when the total flow rate of argon or nitrogen as the carrier and auxiliary gases was kept constant, but the presence of carrier gas for over 5.0 l min^{-1} caused a gradual decrease in the reproducibilities of the fluorescence signals. Below 3.0 l min^{-1} of the carrier gas the fluorescence signal was broadened because of the slower introduction of arsine into the flame. The optimum flow rate is shown in Table 2.

Effect of Pressure in Collection Vessel. The pressure of the arsine and hydrogen generated in the reaction flask (21 in Fig. 2) was indicated with a pressure gauge (24 in Fig. 2). The effect of the pressure in the range from 10 to 40 kPa on the fluorescence signals for arsenic was examined with the nondispersive system in the argon(entrained air)–hydrogen flame. The optimum pressure was found to be 30 kPa. The pressure increased proportionally with an increase in the reaction time. In this work it was considered to be preferable to allow the reaction to continue until the pressure had attained to 30 kPa rather than to monitor the reaction time. At higher pressures, the precision in the fluorescence measurements became poor because the higher pressures resulted in unstability in the flame because of the disturbance of the carrier gas stream.

Effect of Acids. The effects of nitric, perchloric, phosphoric, and sulfuric acids in the range from 0.05 to 2.0 mol dm^{-3} on the fluorescence signal of arsenic were examined. As a consequence, it was found that perchloric, phosphoric, and sulfuric acids did not interfere, but nitric acid caused a large depressing interference. This interference may be attributed to the strong oxidizing action of nitric acid depressing the generation of arsine.

Effect of Various Other Elements. With the arsine-generation technique, most of the interference might be related to the process of reducing arsenic to arsine in both the atomic absorption and atomic fluorescence methods. The effects of 37 elements at the level of a 1000-fold excess were examined in a solution containing 400 ng of arsenic with the nondispersive system and the argon(entrained air)–hydrogen flame. The results are summarized in Table 4, in which the reaction time required to reach a pressure of 30 kPa is also shown for the elements investigated. A large number of elements including other hydride-formimg elements, such as antimony, bismuth, selenium, and tellurium, had great depressing interferences.

It has been reported that bismuth fluorescences at 206.170, 269.7, and 302.5 nm excited with the iodine line at 206.163 nm can be observed.[34,35] A strong emission of the iodine line was observed in the arsenic electrodeless discharge lamp used. However, no enhancement in the fluorescence signal with the nondispersive system was observed in the presence of bismuth. This means that hardly no bismuth hydride(bismuthine) is produced by the zinc reduction method under the conditions suitable for arsenic.

Analytical Working Curve, Sensitivity, and Precision. Analytical working curves were obtained by using arsenic standard solutions freshly prepared from a 1000 ppm stock solution with both the nondispersive and dispersive systems in both the hydrogen flames. Figure 4 shows the analytical working curves thus obtained. The lower limits of the linear range in the curves were severely restricted by the relatively high background due to the reagent blank, as is shown in Fig. 4. The reagent blank was approximately 20 ng of arsenic in 20 ml of a sample. As has previously been reported by Dagnall *et al.*,[1] the 193.7 nm line was more sensitive at lower concentrations of arsenic than the 197.2 nm line.

The detection limits, expressed by the mass or concentration which produces a fluorescence signal equal

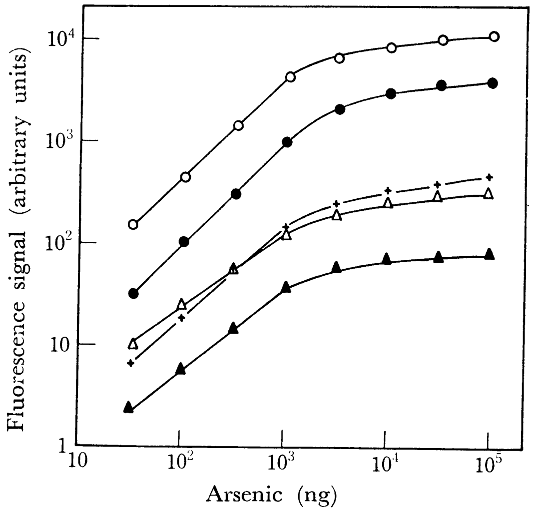

Fig. 4. Analytical working curves for arsenic in atomic fluorescence spectrometry.
○: With nondispersive system in argon (entrained air)-hydrogen flame, ●: with nondispersive system in nitrogen (entrained air)-hydrogen flame, △: with dispersive system at 193.7 nm in argon (entrained air)-hydrogen flame, +: with dispersive system at 197.2 nm in argon (entrained air)-hydrogen flame, ▲: with dispersive system at 193.7 nm in nitrogen (entrained air)-hydrogen flame.

TABLE 5. DETECTION LIMITS OF ARSENIC BY ATOMIC FLUORESCENCE

Flame	Detection limit[a]			
	Nondispersive system		Dispersive system[b]	
	ng	ppb	ng	ppb
Ar(air)-H_2[c]	2.3	0.12	15.2	0.76
N_2(air)-H_2[d]	4.8	0.24	31.1	1.56

a) Signal-to-noise ratio=2. b) At 193.7 nm. c) Argon (entrained air)-hydrogen flame. d) Nitrogen (entrained air)-hydrogen flame.

to twice the noise level(signal-to-noise ratio=2), are shown in Table 5. The detection limits with the dispersive system were obtained at 193.7 nm.

Standard solutions containing 30, 100, 300, and 1000 ng of arsenic were prepared, and the fluorescence signals were repeatedly measured with the nondispersive system in the argon(entrained air)–hydrogen flame. The relative standard deviations, calculated from seven measurements, were 11.5, 8.9, 4.2, and 2.7% for 30, 100, 300, and 1000 ng of arsenic respectively.

Application to the Determination of Arsenic in Wastewaters. The present method was also applied to the determination of arsenic in wastewaters. The wastewater samples were taken at the inlet of the Wastewater Treatment Facility of the University of Osaka Prefecture. The most sensitive nondispersive atomic fluorescence measurements were made with the argon (entrained air)–hydrogen flame under the optimum conditions shown in Table 2. The samples were diluted by a factor of 2 to adjust the concentrations of sulfuric and hydrochloric acids to 5 and 20% respectively. The results thus obtained are shown in Table 6. The atomic absorption measurements at 193.7 nm in the argon(entrained air)–hydrogen flame with a long-path "multi-flame" burner[29,30,36–38] instead of the burner newly constructed for the atomic fluorescence measurements were made by means of the same procedures as in the atomic fluorescence method. The results obtained by the atomic fluorescence method were in good agreement with those obtained by the atomic absorption method.

TABLE 6. DETERMINATION OF ARSENIC IN WASTEWATERS

Sample	Arsenic (ppb)[a]	
	Atomic fluorescence spectrometry[b]	Atomic absorption spectrometry
1	11	12
2	14	16
3	18	21
4	10	9
5	469	453
6	28	30
7	116	124
8	22	24
9	90	83
10	58	54

a) Average for five determinations. b) With the nondispersive system in argon (entrained air)-hydrogen flame.

Conclusion

The present nondispersive and dispersive atomic fluorescence spectrometers have been proved to be sensitive and reliable for the determination of arsenic at the nanogram order. The detection limits obtained with the nondispersive system and the argon(entrained air)–hydrogen flame produced by using a newly constructed burner were comparable with those reported by other authors.[26,27] In this study the sensitivity obtained by the nondispersive system was about one order of magnitude better than that obtained by the dispersive system at 193.7 nm. The former system requires a considerably simpler and less expensive instrumentation than the latter system. Moreover, there is little or no spectral interference except for the presence of the other hydride-forming elements examined in the present study, because of the separation of the analyte from the solution prior to atomization in the flame.

It was verified that the most sensitive nondispersive atomic fluorescence spectrometry can give a lower detection limit and a much larger linear dynamic range for arsenic than the corresponding atomic absorption spectrometry. With respect to interference, however, the present system was similar to the atomic absorption spectrometry.

An improvement in the sensitivity and linear dynamic range of arsenic might be made with a nonflame atomizer as an atom reservoir and/or the sodium tetrahydroborate($NaBH_4$) reduction method, which gives a much lower reagent blank than the zinc tablet reduction combined with tin(II) chloride and potassium iodide. Work is currently under way in this laboratory to investigate this possibility.

References

1) R. M. Dagnall, K. C. Thompson, and T. S. West, *Talanta*, **15**, 677 (1968).

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

3) R. M. Dagnall, M. R. G. Taylor, and T. S. West, *Spectrosc. Lett.*, **1**, 397 (1968).

4) K. C. Thompson and P. C. Wildy, *Analyst(London)*, **95**, 776 (1970).

5) A. Fulton, K. C. Thompson, and T. S. West, *Anal. Chim. Acta*, **51**, 373 (1970).

6) M. S. Cresser and T. S. West, *Anal. Chim. Acta*, **51**, 530 (1970).

7) T. J. Vickers, P. J. Slevin, V. I. Muscat, and L. T. Farias, *Anal. Chem.*, **44**, 930 (1972).

8) W. B. Barnett and H. L. Kahn, *Anal. Chem.*, **44**, 935 (1972).

9) P. L. Larkins, *Spectrochim. Acta, Part B*, **26**, 477 (1971).

10) R. M. Dagnall, M. R. G. Taylor, and T. S. West, *Lab. Pract.*, **20**, 209 (1971).

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

12) E. F. Dalton and A. J. Malonoski, *At. Absorpt. Newsl.*, **10**, 92 (1971).

13) R. C. Chu, G. P. Barron, and P. A. Baumgarner, *Anal. Chem.*, **44**, 1476 (1972).

14) Y. Yamamoto, T. Kumamaru, Y. Hayashi, and T. Kamada, *Bunseki Kagaku*, **22**, 876 (1973).

15) T. Maruta and G. Sudoh, *Anal. Chim. Acta*, **77**, 37 (1975).

16) S. Terashima, *Anal. Chim. Acta*, **86**, 43 (1976).

17) Y. Yamamoto and T. Kumamaru, *Z. Anal. Chem.*, **281**, 353 (1976).

18) F. J. Schmidt and J. L. Royer, *Anal. Lett.*, **6**, 17 (1973).

19) F. J. Fernandez, *At. Absorpt. Newsl.*, **12**, 93 (1973).

20) K. C. Thompson and D. R. Thomerson, *Analyst (London)*, **99**, 595 (1974).

21) A. E. Smith, *Analyst(London)*, **100**, 300 (1975).

22) F. D. Pierce, T. C. Lamoreux, H. R. Brown, and R. S. Fraser, *Appl. Spectrosc.*, **30**, 38 (1976).

23) J. Agget and A. C. Aspell, *Analyst(London)*, **101**, 341 (1976).

24) F. D. Pierce and H. R. Brown, *Anal. Chem.*, **49**, 1417 (1977).

25) E. N. Pollock and S. J. West, *At. Absorpt. Newsl.*, **12**, 6 (1973).

26) K. Tsujii and K. Kuga, *Anal. Chim. Acta*, **72**, 85 (1974).

27) K. C. Thompson, *Analyst(London)*, **100**, 307 (1975).

28) T. Nakahara, T. Tanaka, and S. Musha, *Bull. Chem. Soc. Jpn.*, **51**, 2020 (1978).

29) T. Nakahara, H. Date, M. Munemori, and S. Musha, *Bull. Chem. Soc. Jpn.*, **46**, 637 (1973).

30) T. Nakahara, H. Nishino, M. Munemori, and S. Musha, *Bull. Chem. Soc. Jpn.*, **43**, 1706 (1973).

31) P. J. T. Zeegers, R. Smith, and J. D. Winefordner, *Anal. Chem.*, **40**, 26A (1968).

32) J. D. Winefordner and R. C. Elser, *Anal. Chem.*, **43**, 24A (1971).

33) G. F. Kirkbright and T. S. West, *Chem. Brit.*, **8**, 428 (1972).

34) R. M. Dagnall, K. C. Thompson, and T. S. West, *Talanta*, **14**, 1467 (1967).

35) R. S. Hobbs, G. F. Kirkbright, and T. S. West, *Talanta*, **18**, 859 (1971).

36) T. Nakahara and S. Musha, *Anal. Chim. Acta*, **75**, 305 (1975).

37) T. Nakahara and S. Musha, *Anal. Chim. Acta*, **80**, 47 (1975).

38) T. Nakahara and S. Musha, *Appl. Spectrosc.*, **29**, 352 (1975).