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Flameless Atomic Fluorescence Spectrometry of Mercury by Dispersive and Nondispersive Systems in Combination with Cold-vapor Technique

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An atomic fluorescence spectrometer with dispersive and nondispersive systems has been designed and constructed. A flameless atomic fluorescence spectrometric method with the newly constructed spectrometer is described for the determination of mercury at the nanogram level. Mercury is reduced by tin(II) chloride and released from solution by a stream of argon into a quartz fluorescence cell. The fluorescence signal is measured by dispersive and nondispersive systems. Linear analytical working curves covering the mass range of mercury from the detection limits to approximately 10 and 1 μg have been established with dispersive and nondispersive systems, respectively. With the nondispersive system a detection limit of 0.003 ppb or 0.05 ng of mercury could readily be obtained. The present method was satisfactorily applied to the determination of mercury in wastewater samples.

As with atomic absorption spectrometry, atomic fluorescence spectrometry of mercury has been carried out both with flame and flameless vaporization(atomization) techniques. Atomic fluorescence spectrometric determination has some advantages over atomic absorption spectrometry, for example, a wider dynamic range not limited by the Lambert-Beer law, less susceptibility to interferences from spurious vapors, and a much greater possibility for simultaneous multi-element determination.

Mercury determination using atomic fluorescence spectrometry have been described by Winefordner and co-workers,1–6) West and co-workers,7–10) Vickers and co-workers,11–13) Larkins,14) and Vitkun *et al.*15) using a flame as an atom reservoir. Muscat and co-workers,16,17) Thompson and co-workers,18,19) Shimomura and Hiroto,20) Hawley and Ingle,21) Cavalli and Rossi,22) and Caupeil *et al.*23) used a flameless cold-vapor technique. In the latter instances, the mercury reduced from solution has been excited in a fluorescence cell(quartz or quartz-windowed);16,17,21) some workers18–20,22,23) have eliminated the cell completely and vented the mercury vapor into the atmosphere where fluorescence excitation occured. Some authors24,25) have used a flameless method of pulsed thermal atomization. For fluorescence measurements, a nondispersive system for atomic fluorescence spectrometry has certain advantages over a dispersive system such as greater energy throughput, simpler instrumentation, and simultaneous measurement of multiple lines of the analyte. In the case of flameless methods for mercury a nondispersive system might be preferable to a dispersive system, since mercury is mostly separated from the interfering matrix in the solution prior to fluorescence measurements. However a satisfactory detection limit for a nondispersive system has not always been substantiated in the literature concerning mercury.1–25) Some authors19,22,23) have reported the detection limits of 0.02—0.05 ng of mercury by using a cold-vapor technique. Until recently, the best reported detection limits21) were 0.005 ppb or 0.005 ng of mercury, obtained with a dispersive system and a cold-vapor technique.

The present authors have designed and constructed an atomic fluorescence spectrophotometer which can be used with both dispersive and nondispersive systems. This paper describes the performance of the newly constructed atomic fluorescence spectrometer with which the atomic fluorescence of mercury has been measured using a cold-vapor technique. The present method has been successfully applied to the determination of mercury at the ppb level in wastewater samples.

Experimental

Chemicals. The mercury stock solution of Hg(II), 1000 ppm, was prepared from analytical-reagent grade $HgCl_2$, nitric acid and distilled water. Each mercury solution was prepared just before use from a 10-ppm solution of mercury which was prepared daily from the stock solution. The tin(II) chloride solution was prepared by dissolving tin(II) chloride (10 g) in hydrochloric acid(50 ml) and then by diluting to 100 ml with distilled water. The tin(II) chloride solution was bubbled with mercury-free argon, nitrogen or air to remove any mercury contamination. Magnesium perchlorate was used for drying the mercury vapor produced and granular activated charcoal for removing any trace amounts of mercury from argon, nitrogen or air. All the chemicals used in this study were obtained from Wakô

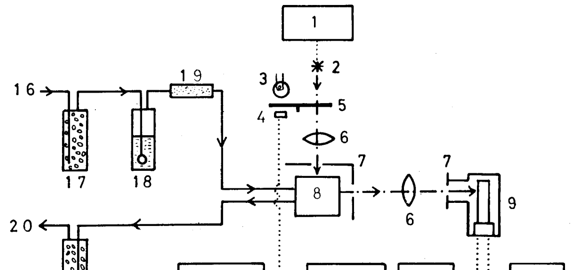

Fig. 1. Block diagram of the nondispersive atomic fluorescence spectrometer.

1: Power supply, 2: light source, 3: small lamp, 4: photocell, 5: light chopper, 6: lenses, 7: diaphragms, 8: fluorescence cell, 9: photomultiplier and its housing, 10: high voltage power supply, 11: preamplifier, 12: lock-in amplifier, 13: power stabilizer 14: recorder, 15: oscilloscope, 16: carrier gas inlet, 17: activated charcoal traps, 18: reduction vessel, 19: drying tube, 20: carrier gas outlet, ——: carrier gas flow, ———: optical path, ······: electrical line.

Table 1. Experimental components used in this study

Item	Description (model No.) and supplier
Power stabilizer	A-133, NF Circuit Design Block
Light source	
Hg pen lamp	11SC-2, Ultra-Violet
Power supply	SCT-1, Ultra-Violet
Hg electrodeless discharge lamp	Hg metal (12 mg), Ar 6.7×10^2 Pa, 8 mm i. d.×50 mm long (Suprasil), Laboratory-made
Power supply	Microtron 200, Electro-Medical Supplies
Resonant cavity	Model 211L, Electro-Medical Supplies
Lens	30-mm diameter, 75-mm focal length, quartz
Fluorescence cell	$25\times25\times30$ mm^3 and $12\times12\times30$ mm^3, quartz
Monochromator	JE-30, Nippon Jarrell-Ash
Entrance slit width	0.5 mm
Exit slit width	0.5 mm
Photomultiplier	R-166 (for nondispersive system), R-106 UH (for dispersive system), Hamamatsu TV
High voltage power supply	412B, John Fuke
Preamplifier	JP 406, Nippon Jarrell-Ash
Operational amplifier	2F/4539B, Aikoh Electric
Power supply	±15 V, Laboratory-made
Lock-in amplifier	572B, NF Circuit Design Block
Oscilloscope	CS-1351, Trio
Recorder	QPD_{54}, Hitachi
Flow regulator	LAS-S301, Nippon Tokushu Keiki
Reduction vessel	Volume 30 ml, Kinoshita

Pure Chemicals Co.

Apparatus. The block diagram of the newly constructed atomic fluorescence apparatus for a nondispersive system is shown in Fig. 1. The specific components employed are summarized in Table 1. The right half of Fig. 1 shows an atomic fluorescence spectrometer with a fluorescence cell. For a dispersive system the photomultiplier and its housing in Fig. 1 are replaced by the monochromator equipped with another type of photomultiplier.

Fluorescence Cell. Two fluorescence cells, being similar to that previously reported,[16)] were made from transparent quartz. The square cells have 1.2×3- and 2.5×3-cm^2 quartz windows on two adjacent sides. The other two-adjacent sides of the cells were blackened by lusterless paint. The fluorescence cell was heated to approximately 120 °C by a ribbon heater to prevent the deposition of water onto the inner surface of the cell. For inlet and outlet ports, the glass tubing of 6 mm inside diameter was connected to the top and bottom of the cell. The connections between the fluorescence cell, magnesium perchlorate drying tube, reduction vessel, and activated charcoal bottles(Fig. 1) were made from silicon rubber tubing of 5 mm inside diameter.

Preparation of Mercury Electrodeless Discharge Lamps. A microwave-excited electrodeless discharge lamp(EDL) is known to be one of the most useful spectral line sources for atomic fluorescence spectrometry.[26–29)] The authors prepared a number of Hg-EDLs using a vacuum line as illustrated in Fig. 2. The EDL-blank was made from transparent quartz ("suprasil") tubing of 8-mm internal diameter and 1-mm wall thickness. A 15-cm length of quartz tubing was sealed at one end and a constriction made between 1 and 7 cm from the end to give a tube from 1 to 7 cm in length. The tubing, the other end of which had a 12/20 mm ground glass socket, was attached to one of the outlets on the vacuum line and pumped down to a pressure of approximately 9.3×10^{-2} Pa. Argon was then introduced into the system and it was again pumped down to a similar pressure. The quartz tube(EDL-blank) was then heated to just below its melting point for about 5 min, during which time argon was again introduced into the system and pumped out. This procedure was repeated three times. The tube was allowed to cool under vacuum and then removed from the line. Between 5 and 20 mg of mercury metal was introduced into the tube, which was then reconnected to the vacuum line. The tube was evacuated as before, flushed out with argon, and re-evacuated to a pressure of about 9.3×10^{-2} Pa. Very gentle heating was then applied to the tubing to drive off any moisture or occluded gases in the mercury. The system was flushed twice more with argon and finally a given pressure was introduced into the vacuum system and the constriction sealed by an

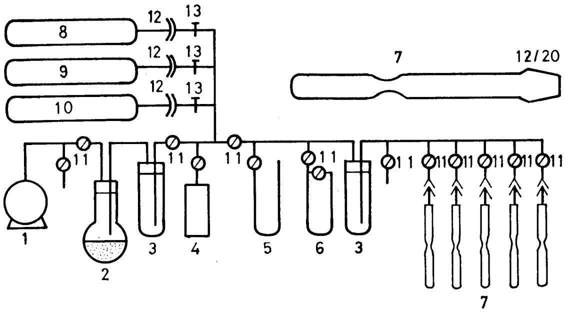

Fig. 2. Vacuum system used for preparation of electrodeless discharge lamps.
1: Mechanical pump, 2: diphosphorus pentaoxide trap, 3: liquid-nitrogen cold trap, 4: vacuum gauge, 5: mercury manometer, 6: oil manometer, 7: lamp blanks, 8: argon reservoir, 9: neon reservoir, 10: helium reservoir, 11: vacuum stopcocks, 12: ball-type joints, 13: needle valves.

Table 2. Optimum experimental conditions

Light source	Hg electrodeless discharge lamp
Microwave power	19 W (incident power, 25 W; reflected power, 6 W)
RC time constant	1.0 s
High voltage for photomultiplier	800 V
Load resistor	470 kΩ
Modulation frequency	90 Hz (for nondispersive system), 240 Hz (for dispersive system)
Fluorescence cell	$25 \times 25 \times 30$ mm^3
Diaphragms	
For cell	20×20 mm^2
For detection system	8×15 mm^2 (for dispersive system), 2×5 mm^2 (nondispersive system)
Carrier gas	Argon
Flow rate	1.0 l min^{-1}
Drying tube	9 cm long $\times$ 3 cm diameter
Volume of sample	20 ml
Volume of reductant	1.0 ml (10% $SnCl_2$-6 M HCl)

oxygen-propane hand torch.

Initiation of the discharge in the resonant cavity was achieved with a simple Tesla coil vacuum tester. The most useful Hg-EDL employed throughout this study is shown in Table 1.

General Procedure. A fixed volume(20 ml) of a mercury solution was introduced into the reduction vessel where the ionic mercury was reduced to mercury vapor by tin(II) chloride. The mercury vapor was then quickly carried by a stream of mercury-free argon, nitrogen or air through a glass tube with a spherically sintered glass end, which was connected to the fluorescence cell *via* a magnesium perchlorate drying tube (Fig. 1). There, a fluorescence signal was instantaneously generated. The height of the recorded peak was a measure of the mercury concentration.

Table 2 shows the optimum oprating conditions for the flameless atomic fluorescence spectrometry of mercury with both the dispersive and nondispersive systems.

Results and Discussion

Effect of Diaphragms in the Optics. The constant background level was mainly attributed to direct specular reflection and scattering of light from the mercury lamp into the fluorescence measuring entry aperture. This background was carefully minimized by placing diaphragms in front of two adjacent windows of the fluorescence cell and the entrance slit of the monochromator for the dispersive system and the photomultiplier housing for the nondispersive system. For maximum sensitivity it was essential to minimize the background level. In this study a number of rectangular or square diaphragms were used; at the same time the fluorescence signal and the background level were measured with each diaphragm to maximize the signal-to-noise ratio for the mercury determination. The optimum sizes of the diaphragms employed are shown in Table 2.

Effect of Modulation Frequencies of Source Radiation. In this study two types of light choppers were used for modulation of the source radiation; one was for 14.4 and 28.8 Hz and the other for 90, 150, 240, 480, and 960 Hz. The former had a synchronous motor (Japan Servo Co., Type HM6P2D1) of 30 Hz with a 1/12.5 reduction gear (Japan Servo Co., Type 6G12.5 H). The latter had a synchoronous motor (Yokogawa Sertec Co., Type SM-D3N) of 30 Hz. The relationships between relative fluorescence intensities and modulation frequencies were obtained for both the dispersive and the nondispersive systems and are shown in Table 3. The differences in relative fluorescence intensities may be attributed to the frequency characteristics of the photomultipliers and to the precision of the sectors, especially at the higher frequencies. The sectors used in the light choppers were all handmade. The optimum frequencies were 90 and 240 Hz for the dispersive and the nondispersive systems, respectively.

Table 3. Effect of modulation frequencies on fluorescence signals

Frequency (Hz)	Relative fluorescence signal[a]	
	Nondispersive system	Dispersive system
14.4	0.91	0.75
28.8	0.77	0.55
90	1.00	0.79
150	0.84	0.69
240	0.84	1.00
480	0.70	0.69
960	0.11	0.05

a) Mercury of 20 ng.

Table 4. Effect of carrier gas on fluorescence signals

Carrier gas[a]	Relative fluorescence signal[b]	
	Dispersive system	Nondispersive system
Air	1.00	1.00
Nitrogen	5.67	5.57
Argon	20.3	19.5

a) Flow rate of 1.0 l min^{-1}. b) Mercury of 10 ng.

Effect of Carrier Gas. Fluorescence measurements were made using argon, nitrogen, and air as the carrier gas. The enhancement of the fluorescence signals obtained by use of argon, compared with air, was approximately greater by a factor of 20, as shown in Table 4. Argon was the most useful carrier gas for fluorescence measurements taking advantage of its small cross section for the quenching of fluorescence, consequently argon was used throughout this study unless otherwise stated. The effect of carrier gas flow rates was also investigated. The flow rates between 0.4 and 1.4 l min^{-1} did not adversely affect the fluorescence measurements. However a decrease in flow rates caused an increase in half-widths of the fluorescence peaks. An optimum flow rate of 1.0 l min^{-1} was chosen in the following study.

Effect of Microwave Power on Source Radiation and Fluorescence Intensities. In atomic fluorescence spectrometry it is theoretically known that the fluo-

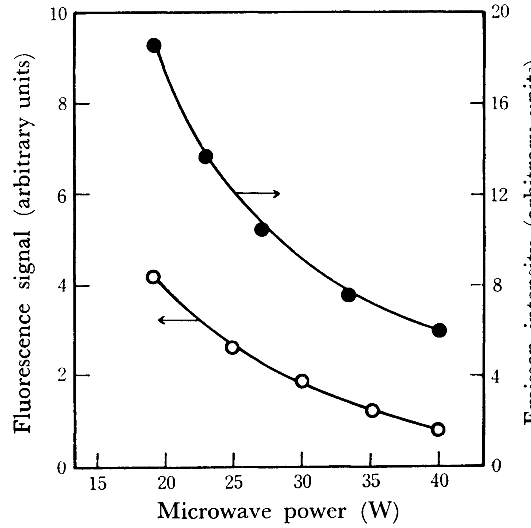

Fig. 3. Effect of microwave power on fluorescence signal and emission intensity of Hg-EDL.
○: Fluorescence signal at 253.7 nm, ●: emission intensity of Hg 253.7-nm line.

Table 5. Effect of organic solvents on fluorescence signals

Amount added (μg)	Relative fluorescence signal[a)] Benzene	Acetone	Ethanol
0	1.00	1.00	1.00
500	1.01	0.97	1.02
1000	0.68	0.80	0.96
2000	0.66	0.76	0.87
5000	0.68	0.86	0.86
10000	0.77	0.80	0.80

a) With the nondispersive system for mercury of 20 ng.

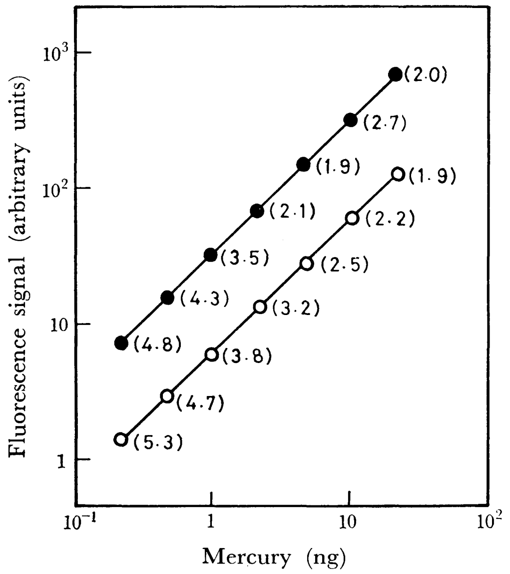

Fig. 4. Analytical working curves for mercury.
●: With nondispersive system, ○: with dispersive system, ( ): relative standard deviations(%).

Table 6. Detection limits for mercury by atomic fluorescence

Carrier gas	Detection limit[a)] Nondispersive system Hg-EDL	Nondispersive system Hg pen lamp	Dispersive system Hg-EDL	Dispersive system Hg pen lamp
Air	1.0 ng	2.0 ng	12.9 ng	23 ng
	0.05 ppb	0.1 ppb	0.65 ppb	1.2 ppb
Argon	0.05 ng	0.1 ng	0.5 ng	2.0 ng
	0.003 ppb	0.05 ppb	0.03 ppb	0.1 ppb

a) $S/N=2$.

rescence intensity is directly proportional to the source radiation intensity.[30–32] The characteristics of the Hg-EDLs prepared were studied in terms of emission intensities and fluorescence signals at various microwave powers. The results obtained are shown in Fig. 3. The microwave power is a net power for discharge, that is, the reflected power is subtracted from the incident power. The optimum power for the Hg-EDL was 19 W; *i.e.*, an incident power of 25 W and a reflected power of 6 W. The Hg-EDL described in Table 1 gave a stable intensity after a warming-up time of *ca.* 30 min during this work and could be used for further experiments.

Quenching of Organic Solvents. The excited atoms are subject to radiationless deactivation due to bimolecular collision with the other species present in the atom reservoir, resulting in a decrease of fluorescence signal.[33] In this study the effect of some organic solvents, *e.g.*, acetone, benzene, and ethanol, was examined in their range of 500 to 10000 μg at a constant mercury level of 20 ng. The results obtained are shown in Table 5. The decrease in fluorescence signals may be attributed mainly to the quenching of fluorescence. The organic solvents(compounds) of more than 1000 μg are thus able to decrease the fluorescence signals, and so the effect of such quenching by organic solvents of higher vapor pressures should be corrected for in the determination of mercury in practical samples.

Analytical Working Curves, Sensitivity, and Presicion. Analytical working curves were obtained by using mercury standard solutions freshly prepared from a 1000-ppm mercury stock solution with both dispersive (at 253.7 nm) and nondispersive systems. A mercury pen lamp was used instead of Hg-EDL because of the much easier operation of the pen lamp. Two typical working curves obtained under the optimum conditions are shown in Fig. 4. The detection limits, expressed as the mass or concentration which produces a fluorescence signal equal to twice the noise level ($S/N=2$), are showed in Table 6. The analytical working curves were linear from the detection limits to approximately 10 and 1 μg of mercury with dispersive and nondispersive systems, respectively. The relative standard deviations for 10 measurements are shown in parentheses for the individual plots in Fig. 4. A blank value was negligible compared with instrumental limitations. The difference in sensitivities between with the Hg-EDL and with the mercury pen

TABLE 7. DETERMINATION OF MERCURY IN WASTEWATERS BY ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION

Sample[a]	Atomic fluorescence	Atomic absorption
A	7.6 ppb	7.3 ppb
B	23.0	22.5
C	3.0	2.8
D	2.2	2.1
E	18.0	16.8
F	21.0	20.8
G	4.0	3.8
H	1.6	2.1

a) Sample taken: 20 ml.

lamp may be explained by the fact that the Hg 253.7-nm line of the former was more intensive by a factor of 1.5 than that of the latter and that in atomic absorption measurements at 253.7 nm the sensitivity for 1% absorption with the former was higher by a factor of 1.4 than that with the latter.

Application of the Present Method to the Determination of Mercury in Wastewaters. The present method was applied to the determination of traces of mercury in wastewaters which were taken at the inlet of the Wastewater Treatment Facility of the University of Osaka Prefecture. The more sensitive nondispersive atomic fluorescence measurements were made using a mercury electrodeless discharge lamp and argon as an excitation source and carrier gas, respectively, under the optimum conditions as is shown in Table 2. The samples were acidified with a few drops of high-purity nitric acid. For atomic absorption spectrometry a quartz absorption cell of 1.8 cm internal diameter and 20 cm length was used as an atom reservoir instead of a fluorescence cell. The procedures for both methods were the same as already mentioned. The results are shown in Table 7. All the analytical results were obtained by referring to each calibration graph and 7 determinations taken and averaged for individual samples. The organic solvents(substances), being soluble in hexane, in the samples were not so much that they produced quenching of fluorescence in the measurements. The results by the present method are in good agreement with those by flameless atomic absorption spectrometry.

Conclusion

The present nondispersive and dispersive atomic fluorescence spectrometer which has been constructed has proved to be sensitive and reliable for the determination of trace amounts of mercury. The detection limits obtained with the nondispersive system were comparable with those obtained by recent authors.[19,21–23] The present detection limits would be improved by decreasing the scattering and reflection of light from the excitation souce into the measuring aperture and by developing the efficiency in light-gathering of the mercury lamp and the fluoresence of mercury vapor. It was impossible to measure the 184.9-nm mercury line of resonance fluoresence with the dispersive system due to appreciable atmospheric absorption at this wavelength. The present system is useful for the determination of traces of mercury in water samples.

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