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Application of a New High Frequency Barium Discharge Lamp to Atomic Absorption Spectrometry

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A new high frequency discharge lamp of barium with a hollow electrode is successfully utilized as the spectral line source of atomic absorption spectrometry. The emission intensity of the new lamp at 553.5 nm operated at 25 W is about twelve times stronger than that of a commercially available dc hollow cathode lamp operated at 20 mA. The new lamp was applied to graphite furnace atomic absorption spectrometry. The detection limit ($S/N=2$) obtained with the new lamp (25 W operation) was $0.0007 \mu\text{g/mL}$, which was about 3 times better than that obtained with the dc hollow cathode lamp (20 mA operation).

1. Introduction

It has already been established that the sensitivity of atomic absorption spectrometry depends on the spectral line width of the atomic resonance line. Although the commercially available hollow cathode lamp has a narrow line width, it sometimes provides a relatively poor intensity at the atomic resonance line.

When the lamp intensity is low, the background radiation from an atom reservoir may be a limiting factor to the detection limit. To overcome this limitation, the use of a high intensity light source in parallel with a narrow band pass setting is desirable.

In graphite furnace atomic absorption spectrometry with a commercially available hollow cathode lamp, barium is known to be one of the elements which are difficult to be de-

termined.

The reasons are as follows; (1) the spectral line intensity of the commercially available hollow cathode lamp is relatively low at the principal resonance line of barium (553.5 nm), (2) the resonance line lies in the relatively long wave-length region, in which molecular emission spectra due to matrix elements are likely to occur, (3) a relatively high furnace temperature (2700°C or more) is required in the atomizing stage. As a result, the high background radiation from the incandescent graphite tube deteriorates the S/N ratio.

A new spectral line source with a hollow electrode, which was operated at high frequency power, was recently developed at our laboratory⁽¹⁾. In a previous paper⁽²⁾, the new high frequency discharge lamps (Cd, Pb, Zn) were successfully applied to atomic fluoresc-

ence measurements, and it was proved that the spectral line width of the resonance lines emitted from the new lamps were narrow enough to be used in the atomic absorption measurements.

This report describes the application of the new lamp to barium analysis by the graphite furnace atomic absorption spectrometry.

2. Experimental

2.1 Apparatus

The construction of the new lamp is shown in Fig. 1. Argon was used as the filler gas, and was maintained at a pressure of 4 Torr. The hollow electrode (inside diameter: 3 mm, length: 15 mm, hollow depth: 10 mm) was made of a barium-magnesium-aluminium alloy. The ring electrode (inside diameter: 7 mm) was made of nickel wire 1 ϕ mm, and was located approximately 5 mm from the hollow electrode. High frequency (20 MHz) power was supplied to the discharge between the hollow and ring electrodes. The hollow electrode is indirectly cooled by water flowing inside a double-walled glass-sylinder to achieve stable operation at high power.

A Perkin Elmer Model 403 atomic absorption spectrometer was used, which was equipped with a nitrous oxide acetylene burner or a HGA 2000 graphite furnace atomizer. The emission intensity from the graphite tube was measured using a Hitachi atomic absorption spectrometer Model 308 coupled with an electrometer (Takedariken Model TR 8651).

Fig. 1. Construction of high frequency discharge lamp.

- (A) Metal cylinder; (B) Hollow electrode; (C) Getter, (D) Ring electrode; (E) Window; (F) Double walled glass cylinder; (G) Water inlet and outlet; (H) Connector.

2.2 Reagents

Barium stock solution (1000 ppm) was prepared by dissolving 99.99% barium carbonate in analytical reagent grade nitric acid, evaporating to dryness and redissolving it in de-ionized water. More dilute standard solutions were prepared as required.

3. Results and discussion

3.1 Emission Intensity Measurement

Emission intensity measurements were carried out under the conditions shown in Table 1 (A). The effect of lamp wattage on barium emission intensity was measured for five barium atomic spectral lines. The results are shown in Fig. 2. The high frequency power for the new lamp quoted in this paper means the net power supplied to the discharge, i.e. the reflected power is subtracted from the incident power. As shown in Fig. 2, the emission intensity increases with increasing lamp wattage.

Table 1. Experimental Conditions

(A) Lamp emission intensity measurement	
Photomultiplier	HTV R 106
High voltage	400 V
Spectral band width	0.3 nm
(B) Flame atomic absorption measurement	
Acetylene flow rate	12.0 l/min
Nitrous oxide flow rate	13.0 l/min
Distance between burner top and beam center	10.0 mm
Analytical line	553.5 nm
Spectral band width	0.4 nm
(C) Graphite furnace atomic absorption measurement	
Argon flow rate	1.0 l/min
Drying	120°C (temp.) 30 s (time)
Ashing	1000°C (temp.) 20 s (time)
Atomizing	2700°C (temp.) 10 s (time)
Analytical line	535.5 nm
Spectral band width	0.4 nm*
	0.14 nm**

* For hollow cathode lamp (20 mA operation)

** For high frequency discharge lamp (25 W operation)

Fig. 2. Effect of power input on emission intensity for new high frequency discharge lamp at different wavelengths. (A) 455.4 nm; (B) 553.5 nm; (C) 350.1 nm; (D) 577.7 nm; (E) 585.0 nm.

The noise level was about 0.3% of the 553.5 nm spectral line intensity and was independent of lamp wattage in the range of 10~30 W. The relative emission intensities among the five atomic spectral lines were almost the same as for a dc hollow cathode lamp (Hitachi Model HLA-3).

The emission intensity level of the new lamp was compared with that of the dc hollow cathode lamp and the incandescent graphite tube. The results are shown in Fig. 3. As seen in the figure, the emission intensity of the new lamp at 553.5 nm operated at 25 W is about twelve times higher than that of the dc hollow cathode lamp operated at 20 mA. It is superior to that of the incandescent graphite tube when the tube temperature is below 2700°C.

Lamp stability was as good as the previous lamps (Cd, Pb, Zn)⁽²⁾, and only a 5 minute warm-up period was required after initiation

Fig. 3. Effect of temperature on emission intensity from furnace at 553.5 nm. The emission intensity levels for the high frequency discharge lamp and the dc hollow cathode lamp are indicated by (A) and (B), respectively.

of the discharge.

3.2 Atomic absorption measurement

Flame atomic absorption measurements were carried out under the conditions shown in Table 1 (B). The relationship between lamp intensity at 553.5 nm and barium absorbance is shown in Fig. 4 for the high frequency lamp and the dc hollow cathode lamp. The unity of relative intensity on the abscissa was defined as the intensity obtained with the dc hollow cathode lamp operated at 20 mA. When

Fig. 4. Effect of lamp intensity on relative absorbance for the barium resonance line observed for the high frequency lamp (A) and the dc hollow cathode lamp (B) at barium concentration of 20 ppm.

using the dc hollow cathode lamp, the barium absorbance began to decrease when the lamp current was increased beyond 20 mA. This decrease is probably related to broadening of the emission line. In contrast, the barium absorbance was constant when the new lamp was used at power levels between 10~30 W. This indicates that the new high frequency discharge lamp emits far more intense radiation at the principal resonance line of barium than the commercially available dc hollow cathode lamp, while maintaining its narrow spectral line width which is ultimately required in atomic absorption spectrometry. Therefore, the new lamp enables one to use a narrower spectral band pass setting; the same output current from the photomultiplier tube was obtained even if the slit width reduced to about one tenth.

The analytical working curves were obtained by graphite furnace atomic absorption measurements. The measuring conditions utilized are shown in Table 1 (C). The pyrolytic graphite coated tube was used, which was made by the procedure described elsewhere⁽³⁾. The analytical working curves were linear up to 1.0 ng and 0.8 ng for the new lamp and the conventional dc hollow cathode lamp, respectively. The detection limit ($S/N=2$) obtained with the new lamp (25 W operation) was 0.0007 $\mu\text{g}/\text{mL}$. This value is about 3 times better than that obtained with the dc hollow cathode lamp, and is superior to the previously reported values of 0.002 $\mu\text{g}/\text{mL}$ ⁽³⁾ and 0.001 $\mu\text{g}/\text{mL}$ ⁽⁴⁾.

3.3 Application to practical analysis

The new barium lamp was applied to the determination of the barium content in potassium carbonate. Concurrently the accuracy of the procedure was evaluated by adding known amounts of barium to a sample of potassium carbonate. A sample of 0.5 g was weighed exactly, dissolved in 2 mL of 6N nitric acid. A 0.5~2.0 μg of barium was added to a sample

Table 2. Results of determination of barium in reagent (potassium carbonate)

Sample No.	Sample taken (g)	Ba added (μg)	Ba found* (μg)	R. S. D. (%)	Recovery (%)
A	0.5	—	0.61	4.5	—
	0.5	0.50	1.10	4.3	98
	0.5	1.00	1.63	3.0	102
B	0.5	—	1.48	4.3	—
	0.5	1.00	2.48	3.8	99
	0.5	2.00	3.54	4.0	103

* average of five determinations

R. S. D.: Relative standard deviation

and diluted to 5 mL. A 10 μL sample of the solution was taken with an Eppendorf pipette, and the atomic absorption signals were measured under the conditions shown Table 1 (C). The results are shown in Table 2. The relative standard deviation and the recovery were in the range of 3~4.5% and 98~103%, respectively.

4. Conclusion

The new high frequency discharge lamp of barium is useful as a light source for atomic absorption spectrometry, because of the high stability, the high intensity and the narrow line width.

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