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A MICROSAMPLING TECHNIQUE UTILIZING AN ELECTROTHERMAL TUNGSTEN-BOAT VAPORIZATION DEVICE FOR ATMOSPHERIC PRESSURE HELIUM MICROWAVE-INDUCED PLASMA EMISSION SPECTROMETRY

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A discrete microsampling technique using an electrothermal tungsten-boat vaporization device has been applied to atmospheric pressure helium microwave-induced plasma emission spectroemtry. The detection limits of 10^{-10}-10^{-9} g were obtained for Cd, Cu, Fe, Pb, Zn, and P, and the reproducibilities were in the range of 2.4-11.4 %.

An atmospheric pressure helium microwave-induced plasma (MIP) has some advantages as an excitation source for emission spectrometry.[1,2] The plasma excitation energy is large so as to detect the emission signals of most elements including nonmetallic elements with high sensitivity in the conventional UV and visible region.[3] Furthermore, the microwave power required for stable operation is relatively low (generally lower than 100 W). Thus the MIP has been increasingly applied to the analysis of various samples.[4-13] The helium plasma operated at low power, however, does not allow direct introduction of liquid samples because of difficulty in sustaining the plasma.[5,10,13] Therefore, most use of the MIP has been limited to the volatile compounds which can be introduced into the plasma by gas generation or gas chromatographic technique.

The electrothermal atomization is a popular analytical technique in atomic absorption and fluorescence spectrometry. In this technique, various atomization devices such as graphite furnace,[14-17] graphite rod[18-20] or tantalum filament,[21] and platinum or tungsten wire loop[22] have been developed instead of the chemical flames. The combination of the helium MIP and the electrothermal atomizer has a possibility to overcome the difficulty of sample introduction in MIP emission spectrometry, since only the dried analyte vapor is let into the plasma. Hence, in this paper some preliminary experiments using the combined system of the helium MIP and tungsten (W)-boat vaporization device are reported as a convenient microsampling technique.

All chemicals used were of analytical reagent grade. The stock solutions of metallic elements were prepared by dissolving each metallic compound in dil.

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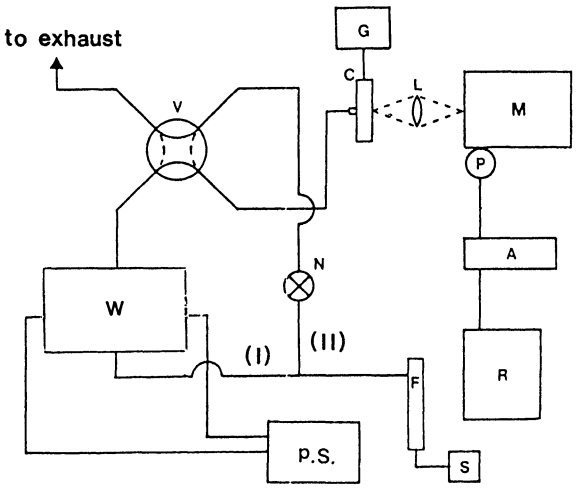

Fig. 1. A schematic diagram of instrumental arrangement.
S: helium gas cylinder,
F: flowmeter,
P.S.: power supply,
N: control valve,
W: vaporization device (*See* Fig. 2),
V: four-way valve,
G: microwave generator,
C: microwave cavity,
L: lens,
M: monochromator,
P: photomultiplier,
A: picoammeter,
R: chart recorder.

Table 1. Instrumental components and operating conditions.

Microwave generator	Ito Chotampa Co. 2.45 GHz, 20-200 W
TM_{010} mode cavity	laboratory constructed
Monochromator	0.5 m Ebert type from Nippon Jarrell-Ash Co. slit widths of both entrance and exit slits; 10 μm
Photomultiplier	R955 from Hamamatsu TV Co.
Tungsten-boat furnace	55 mm x 7 mm, 0.2 mm thick, from Daini Seiko-sha Co.
Power supply	Daini Seiko-sha SAS-714

nitric acid solution. The stock solution of phosphorus was prepared by dissolving potassium dihydrogen phosphate in distilled water.

A schematic diagram of the present system is illustrated in Fig. 1. The instrumental components are also listed in Table 1. The microwave generator was generally operated at 75 W (reflected power; less than 10 W). A quartz tube with 6 mm o.d. and 3 mm i.d. was used as a plasma discharge tube. The W-boat vaporization chamber and the plasma discharge tube were connected with a transfer vinyl tube (6 mm i.d., 8 mm o.d., 4 m long). Two helium gas flows were employed in this experiment, and both of the gas flow rates were adjusted at 0.5 l/min. As the W-boat vaporization device, shown in Fig. 2, the metal atomizer originally developed for atomic absorption spectrometry was conventionally used with some modification. The cover of cylindrical pyrex glass, which had a hole of 30 mm diameter on the top, was placed on the base plate to construct a vaporization chamber. Helium gas blew up from the holes under the W-boat vaporizer through the base plate.

In the experimental procedure, the helium gas line (I) was first set to flow through the W-boat vaporization chamber into the plasma. After the plasma was stabilized, the spectrometer was adjusted at the desired wavelength by using a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL) of each analytical element. Then the four-way valve was turned to connect the helium gas line (I) to the exhaust through the vaporization chamber, and the helium gas line (II) was connected to the plasma directly in order to keep the plasma sustaining. The

silicone rubber septum with a funnel was taken off from the vaporization chamber, and 10 μl of an aqueous sample was applied on the W-boat. After the silicone rubber septum was reset on the chamber, air was purged from the chamber with helium gas, and then the W-boat vaporizer was heated at 150 °C for 60 s (drying step) in order to evaporate solvent to the exhaust. After vaporizing the solvent from the chamber, the four-way valve was returned to the initial position. The W-boat vaporizer was heated at 250 °C for 60 s (ashing step), and then at 2100 °C for 5 s (vaporizing step). The support gas led the vaporized analyte into the plasma and the emission signal was measured. Approximately 10 to 15 samples could be analysed within one hour. One W-boat filament was available about 500 times repeatedly.

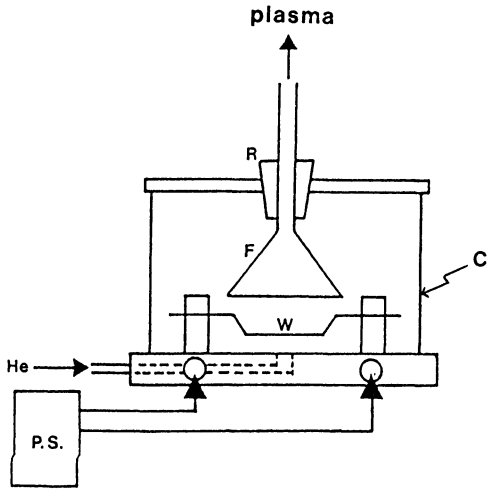

Fig. 2. Tungsten-boat vaporization device. P.S.: power supply, W: tungsten-boat filament, F: funnel, R: silicone rubber septum, C: chamber.

Table 2. Detection limits and reproducibilities.

Element	Wavelength nm		MIP Detection limit (ng)	MIP Reproducibility (%)	ICP[a] Detection limit (ng)
Cd	I	228.8	0.50	5.0	0.03
Cu	I	324.7	0.65	11.4	0.02
Fe	I	248.3	0.50	5.7	---
	II	259.9	1.0	13.8	0.03
Pb	I	261.3	0.10	5.8	---
	II	220.3	---	---	0.2
Zn	I	213.8	0.40	3.7	0.02
P	I	213.6	0.66	2.4	---

a) Values obtained by using the W-boat vaporization device in similar way to the present work.[23]

The detection limits and reproducibilities obtained for some elements are summarized in Table 2. The detection limits represent the absolute amount of analyte corresponding to the signal level which is twice the standard deviation of the blank emission signal at the analyte wavelength. The detection limits obtained by ICP emission spectrometry using a W-boat vaporization device similar to the present one are also shown in Table 2.[23] As can be seen from Table 2, the detection limits obtained with the MIP are worse by about one order of magnitude than those obtained with the similar ICP method. This is partially because a sample introduction efficiency of the present MIP system is lower than that of the ICP system. The plasma gas flow was 0.5 l/min for the MIP, while it was 1.5 l/min for the ICP. Consequently the signal width was broader in the MIP. Another reason is that rather high blank emission signal due to tungsten from the W-boat

vaporizer was observed in the measurement with the MIP, while the blank emission signal was very small in the ICP. In the case of the ICP, a little amount of hydrogen gas could be mixed in the plasma gas in order to avoid the vaporization of tungsten oxides due to the oxidation of the W-boat filament. In the case of the MIP, however, it was impossible to mix hydrogen gas with helium gas because of extinction of the plasma.

The reproducibilities were in the range from 2.4 to 11.4%. These values appear to be not so bad in microsampling analysis using an electrothermal vaporization device. The dynamic range of about 2×10^3 was obtained for measured elements except for copper. The calibration curve of copper was not linear above 1.0 μg/ml. This may be caused by adsorption effect inside the transfer tube.

In this experiment, the W-boat furnace was used as a vaporization device without hydrogen gas, so that the blank emission signal due to tungsten oxides could not be eliminated. Other materials, *e. g.*, graphite, for the furnace, which may provide less spectral interference, should be examined. As has been discussed, however, it has been proven that the MIP may be an efficient excitation source for metallic elements as well as nonmetallic elements.

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