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IMPROVEMENT OF DETECTION LIMIT IN UHF PLASMA TORCH EMISSION SPECTROMETRY

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To improve the detection limits in UHF plasma torch emission spectrometry, the flowthrough pattern of the sheath gas pinching the UHF plasma torch was modified. The plasma torch was pinched by inserting spacers between the inner and the outer wall of a double quartz tube holding the plasma torch, to raise the net intensities of the spectral lines and to depress the background intensities.

Three types of plasma have been proposed for the torch of emission spectrometry. They are microwave torch discharge (MTD, or capacitatively coupled microwave plasma; CMP, or microwave induced plasma; MIP), inductively coupled plasma (ICP), and direct current plasma)DCP, or plasma jet). As is well known, the ICP torches have become increasingly popular in analytical chemistry during past decade. Usually a triple quartz tube has been used in case of a conventional ICP. Carrier gas (0.3-1.5 l/min) with the sample aerosol flows upward through the central tube, and coolant gas (10-20 l/min) flows upward through the outer tube. Occasionally, plasma gas (0-1.0 l/min) flows upward through the second tube, especially for non-aqueous solvents. And the coolant gas occurs the vortex flow which has a high ability to pinch the plasma torch. But the disadvantage of all commercially available instruments and of nearly all research units is the relatively high initial costs and operating expenses (because of the argon and the RF power consumption).

Recently, to reduce the argon and the RF power consumption, there have been some reports in designing miniaturized ICP systems. Genna et al.[1)] have improved the coolant gas inlet tube using hydrodynamic techniques to form a stable vortex flow at low gas flows. Savage and Hieftje[2,3)] have developed and descrived a miniature ICP. Allemand et al.[4] have studied an ICP with 13 mm and 9 mm torches and compared these with the conventional 18 mm torch. Kornblum et al.[5] have reduced the argon consumption to one tenth in an ICP by adding a water cooled jaket. The detection limits of these new ICPs were reported, but they were not as good as those of the conventional ICP.

On the other hand, a double quartz tube has been used in a CMP, and the argon and the UHF power consumption is not so high as a conventional ICP. Plasma gas (2-3 l/min) with the sample aerosol flows upward through the central tube. Sheath gas (3-4 l/min) flows upward through the outer tube, and it pinches the plasma torch. In the case of this condition, the stable vortex flow like the coolant gas flow of the Genna's ICP[1] doesn't occur. It seems that this condition affects to pinch the plasma torch and the excitation process. Especially in a CMP, the role of the sheath gas is important because the sample aerosol has a tendency to be swept around the plasma periphery. Therefore the flowthrough pattern of the sheath gas must be improved using the modified double quartz tube.

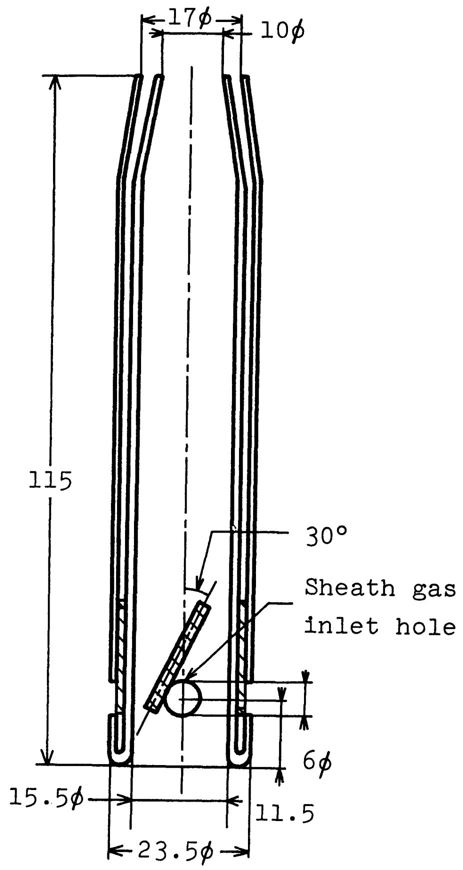

Fig. 1 Modified double quartz tube (mm)

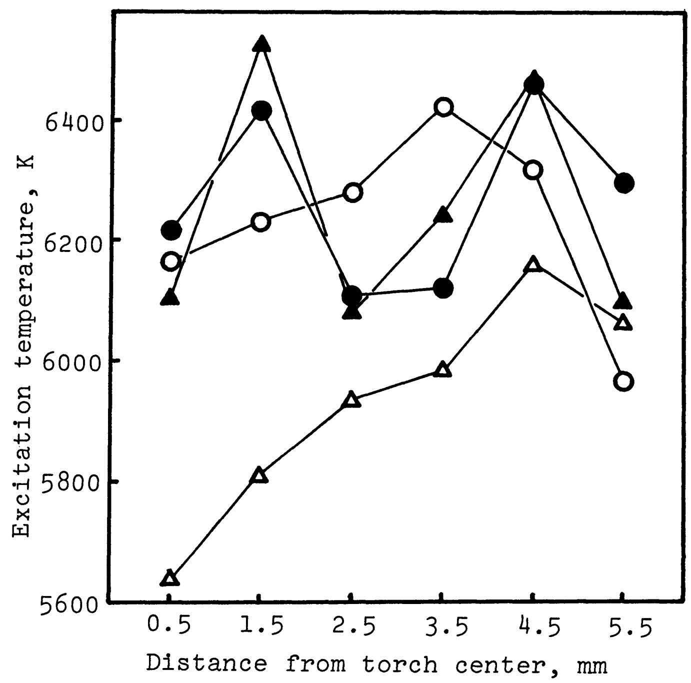

Fig. 2 Effects of double quartz tube on excitation temperature (500 W)

Observation height	Normal	Modified
0 mm	-○-	-●-
5	-△-	-▲-

Hitachi 300 type UHF plasma torch emission spectrometer, a commercially available instrument of CMP, was used in this study, and a new power supplier (2 kV, 330 mA) was connected to an ordinary power supplier (2 kV, 300 mA). The modified double quartz tube is shown in Fig. 1. The spacers of silicone rubber were inserted between the inner and the outer wall of the normal double quartz tube from the four sheath gas inlet holes at an angle of 30 degrees for the vertical. The dimensions of the spacers are as follows. Length : about 20 mm, width : about 2 mm, and thickness : about 1 mm. The position of the spacers inserted and the length of the spacers were examined variously, but the most efficient one is that shown in Fig. 1. In the case of a normal double quartz tube, the sheath gas was introduced to the outer tube through the four gas inlet holes and flowed upward randomly. On the other hand, in the case of the modified double quartz tube, the sheath gas was introduced to the outer tube, collided with the four spacers, and flowed upward with direction. Thus a stable vortex flow was formed. Besides if the gas inlet holes are constricted and the sheath gas is introduced tangentially to increase the swirl velocity of the gas, a more stable vortex flow will be formed.

The distribution of excitation temperature was calculated from the relative intensities of six Fe I lines[6,7]. Avel inversion wasn't perfomed, however, because it was difficult to correct the self-absorption. As shown in Fig. 2, using the normal double quartz tube, the upper the observation height was, the lower was the excitation temperature. On the other hand, using the modified double quartz tube, no decrease of the excitation temperature was observed. The maximum excitation temperature that were observed at 500 W and 700 W are given in Table 1. When the UHF power was 500 W, the excitation temperature using the modified double quartz tube didn't differ much from that using the normal double quartz tube. When the normal double quartz tube was used and the UHF power increased, the plasma torch

Table 1 Effects of UHF power on excitation temperature (K)

Double quartz tube	UHF power 500 W	UHF power 700 W
Normal	6566 ± 107 (n = 13)	6438 ± 82 (n = 7)
Modified	6557 ± 48 (n = 5)	6624 ± 98 (n = 5)

Table 2 Effects of double quartz tube on Y II spectral line intensity

Double quartz tube	Plasma gas flow rate	UHF power 500 W	UHF power 800 W
Normal	3.0 l/min	1.0	4.4
	3.5	1.2	6.7
Modified	3.0	2.3	8.3
	3.5	2.1	11.6

Y II ; 3710.30 Å, Observation height; 5 mm.

became broader and the excitation temperature became lower, although the whole energy of the plasma torch and the net intensities of the spectral lines increased. When the modified double quartz tube was used, however, the excitation temperature became slightly higher with the enhancement of the UHF power. This phenomenon shows that the modified double quartz tube changed the flowthrough pattern of the sheath gas to make the vortex flow more stable.

Table 2 shows the effects of the modified double quartz tube on Y II net intensity. Under the same operating conditions, the relative net intensity was increased from about 1.7 to 2.3 fold by using the modified double quartz tube. To compare with the ordinary conditions (500 W, 3.0 l/min, and a normal double quartz tube), by operating the optimum conditions (800 W, 3.5 l/min, and the modified double quartz tube) the relative net intensity was increased about 12 fold. And then at the UHF power of 1 kW, the relative net intensity was more increased, though the operating time was a few minutes. Using the modified double quartz tube in the determination of phosphorus, the depression of the background deviation was observed; the peak height appeared as background was 8.9 $\pm$ 0.7 mm (relative intensity, n = 10) in this case, against 13.9 $\pm$ 1.8 mm (n = 10) using the normal double quartz tube. In addition, the P I relative net intensity was stronger by 25 %, and so the detection limit was improved (about 0.13 ppm, S/N = 2) and was as good as that of a conventional ICP (2136.20 Å).

In conclusion, by use of the modified double quartz tube, the sheath gas flow became the swirl or vortex flow, and the plasma torch was pinched effectively and stabilized. The plasma stability and the high excitation temperature made the background intensities lower, made the spectral lines intensities higher, and made the detection limits better.

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