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Development of the Sample Introduction Systems for the Analysis of the Powdered Samples in ICP-AES : I. Preliminary Studies (ETV-ICP-AES)

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In the plasma spectrochemical analysis such as inductively coupled plasma (ICP) and direct current plasma (DCP), several different types of nebulizers are used to analyze samples. However, nebulizers commonly used in ICP transport only 2-3% of a sample solution into the ICP, and are susceptible to clogging by suspended particulates and salts. Also greater than 1 mL of liquid sample is required for analysis. On the other hand, because it is impossible to introduce a powdered sample directly into plasma, sample pretreatment is needed. This step inevitably leads to a sample contamination and a decrease of the analyte concentration. Several techniques have been developed to enhance the efficiency of sample introduction to the ICP torch, and so on.[1,2,5,6] Among them, electrothermal vaporizer-inductively coupled plasma (ETV-ICP) has been used to analyze microliter volumes of liquid sample[1~5,11~13] as well as milligrams of powdered samples.[6~10]

In ETV-ICP-AES, because dried aerosols generated by electrothermal heating are introduced into ICP, it is more efficient than conventional method of water aerosols. It consists of several steps to analyze samples in ETV. That is, drying, ashing, atomization, and cleaning steps are involved in sequence. However, the experimental variables, such as current, time, and carrier gas flow rate during drying, ashing, atomization, and clean-up steps, are controlled very precisely to obtain a stable signal.

In our laboratory, the ETV with tungsten filament as a sample introduction method into ICP has been characterized throughly. The various types of sample including aqueous and powdered samples have been analyzed. The experimental results obtained so far will be reported in two papers. Firstly, the better quantitative analytical results of the ETV due to multiple cleaning step are reported in this preliminary report. Contrary to the other studies[1~10] having a single cleaning step after atomization, 5-10 times of multiple cleaning step are applied in this study, hence less memory effect and enhanced reproducibility are observed. Secondly, the experimental results for analysis of powdered samples will be reported in the subsequent paper.

Experimental

ETV used in this work is made at our laboratory, and the schematic diagram is shown in Figure 1. The tungsten filament is bridged between two base electrodes made of copper. The DC power supply (KSC 250, Seoul, Korea Switching Co.) is connected to the base electrodes, and the proper current and voltage for drying and atomization steps are controlled precisely by a computer. For the determination of the reproducibility, 28.5A for 60 seconds and 77.5A for 4 seconds are applied at drying and atomization steps, respectively. After atomization step, the cleaning step is maintained for 4s at 74A and down to 0A, and is repeated 5 to 10 times. Therefore, the memory effect is found to be minimal. The copper base electrodes are cooled by circulating water. Geometrical structure of the cap is maintained dome form, and carrier gas is introduced to tangential direction at the down field of the ETV in order to minimize the condensation onto the inner surface of the cap.

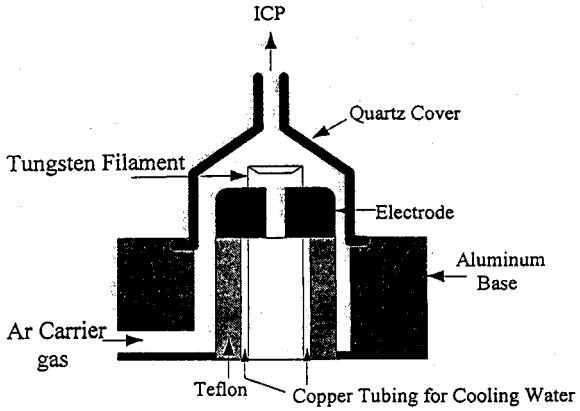

Figure 1. The schematic diagram of electrothermal vaporizer.

The bottles used in this study are soaked in 50% (v/v) hydrochloric acid and nitric acid for a week, then washed with deionized water. After that the bottles are soaked in deionized water for two weeks, and dried for use. 1.0000 g of metallic cadmium is dissolved by 50 mL of hydrochloric acid and diluted quantitatively to a volume of 1 liter. Final concentration of the stock solution is 1000 μg/mL Cd.

Results and Discussion

In general, 5 μL of 1 ppm Cd standard solution was loaded on the top of the tungsten filament (99.999%). The effects of the experimental variables, such as atomization time, observation height, current, acidity, and carrier gas flow rate are investigated on the emission intensity of Cd at 228.82 nm.

Throughout the experiment, the Cd emission intensity is observed at 12 mm above the load coil. First, time for atomization step is varied from 1 to 7 second, while the rest of them are kept constant. The time resolved emission intensities of Cd at 228.82 nm are observed with respect to the different time of the atomization step. As shown in Figure 2, since one second of atomization time is not enough to vaporize the sample, the most of sample is vaporized in the 10 consecutive cleaning steps. As the atomization time is increased from 1 to 4 seconds, the magnitude of the first peak in the cleaning step is greatly reduced. Above using 4 seconds of atomization time, no memory effect is observed in the cleaning step indicating complete vaporization in the atomization step.

The magnitude of current applied to filament is significant

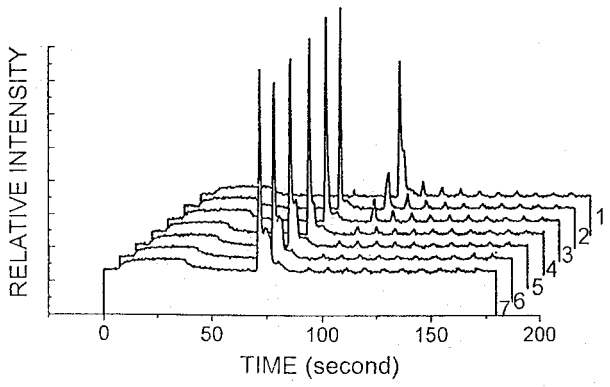

Figure 2. The time resolved emission intensity profiles depending on atomization time.

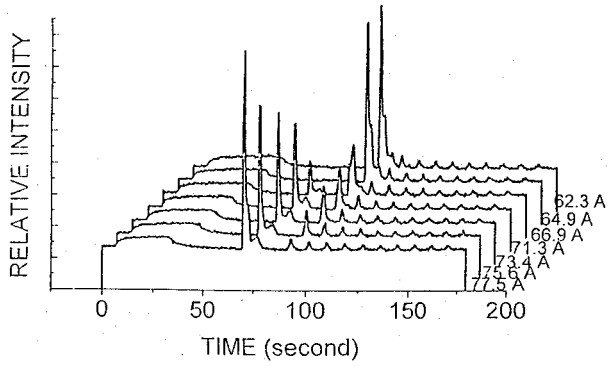

Figure 3. The time resolved emission intensity profiles depending on current.

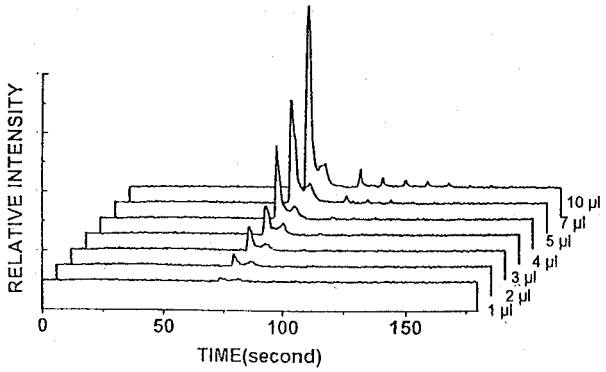

Figure 4. The time resolved emission intensity profiles depending on the amount of sample loaded.

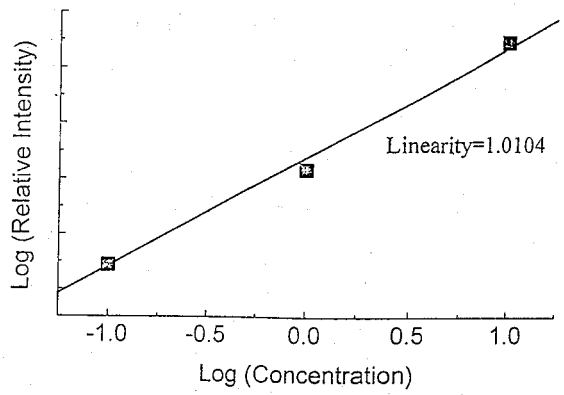

Figure 5. The calibration curve for Cd.

to vaporize the sample. While the current is varied from 62.3 to 77.5 A, 28.5 A is applied for 60 seconds at drying step, and 4 seconds of atomization time is used. As shown in Figure 3, 62.3 and 64.9 A of current is not enough to vaporize the sample in the atomization step. No peak is observed at atomization step. In fact, most of sample is vaporized in the cleaning step. As the current is increased from 66.9 to 77.5 A, the magnitude of vaporization in the atomization step is gradually increased. With 77.5 A of current, the major memory effect is not observed in the 10 consecutive cleaning steps.

In order to investigate the effect of concentration of acid on emission intensity, deionized water, Cd solution of 1 ppm in 2%, 3%, 4%, and 5% nitric acid are introduced. According to the experimental results, the concentration of acid in Cd standard solution is not critical factor to affect the degree of vaporization in the atomization step. As the flow rate of a carrier gas is decreased from 1.1 to 0.3 L/min, the peak width is broaden. The proper flow rate of a carrier gas is found to be 1.1 L/min. Also, the effect of sample volume loaded is observed, and 77.5 A is applied for 4 seconds at atomization step. According to Figure 4, when more than 5 µL of sample is introduced on the filament, the memory effect is observed in the cleaning step. However, less than 5 µL of the sample is not proper to give enough sensitivity, and then 5 µL of the sample is introduced to observe the Cd emission intensity throughout this experiment.

5 µL of sample loaded, 4 seconds of atomization time, 12 mm of observation height, and 77.5 A of current are found to be the optimum conditions of the ETV-ICP-AES. With the optimum conditions, the quantitative analysis of Cd was conducted. Standard calibration curve for 0.1, 1, and 10 ppm Cd is shown in Figure 5. The linearity of calibration curve is found to be 1.0104.

As mentioned before, ETV-ICP-AES has been suffered from the poor reproducibility due to memory and matrix effects. In this study, the reproducibility has been enhanced simply by the multiple cleaning steps. With the optimum conditions, the reproducibilities were determined by 10 consecutive measurements. Due to the irregular shape of the peak, the peak area was used to calculate the reproducibilities. In general, 1-2% of relative standard deviation (RSD) is measured for the analysis of Cd in this study. The enhanced RSD is observed due to minimizing memory effect by using 5-10 times of cleaning steps. Without 5-10 times of cleaning steps, 5-10% of RSD is found, which is comparable to the previous ETV-ICP-AES studies by another researchers.[1~12] However, the shorter lifetime for tungsten filament would be expected.

In conclusion, 5-10 times of multiple cleaning steps after atomization step would be necessary to improve the reproducibility of the quantitative analytical result in ETV-ICP-AES with metal filament.

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