Polymer (Polydimethylsiloxane (pdms)) Microchip Plasma with Electrothermal Vaporization for the Determination of Metal Ions in Aqueous Solution

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We previously reported a 27.12 MHz inductively coupled plasma source at atmospheric pressure for atomic emission spectrometry based on polymer microchip plasma technology. For the PDMS polymer microchip plasma, molecular emission was observed, but no metallic detection was done. In this experiment, a lab-made electrothermal vaporizer (ETV) with tantalum coil was connected to the microchip plasma for aqueous sample introduction to detect metal ions. The electrode geometry of this microchip plasma was redesigned for better stability and easy monitoring of emission. The plasma was operated at an rf power of 30-70 W using argon gas at 300 mL/min. Gas kinetic temperatures between 800-3200 K were obtained by measuring OH emission band. Limits of detection of about 20 ng/mL, 96.1 ng/mL, and 1.01 μg/mL were obtained for alkali metals, Zn, and Pb, respectively, when 10 μL samples in 0.1% nitric acid were injected into the ETV.

Key Words : Microchip plasma, Electrothermal vaporization, Atomic emission, Plasma spectroscopy

Introduction

Various microchip plasmas have been developed for analytical detection sources. These miniaturized sources are versatile and can be used for molecular and atomic emission as well as ionization source for mass spectrometry. The best well-known application for them currently is a GC detector.[1-4] There have been several papers on other microplasma sources based on different kinds of plasma generation techniques.[5-9] Various materials and creative geometries have also been used for performance improvement and miniaturization. In general fused silica capillaries were used for micro plasma generation, and glass or quartz chips were designed for microchip plasmas. However, those materials are difficult to be manufactured and vulnerable to be attacked by fluorine compound. We recently reported a PDMS polymer microchip rf plasma for the detection of fluorinated carbons for the first time.[10] This PDMS microchip can be manufactured easily, is inexpensive, and is more tolerant to plasmas containing fluorocarbons than the silica microchip.

The electrothermal vaporizer (ETV), as a vaporization source, has proven to be a very useful technique for sample introduction in various atomic spectrometry techniques[11-13] because of the higher transport efficiency of dry aerosols, the micro sampling capability,[14,15] and the potential for direct solid analysis and minimal sample pre-treatment.[16-18] All of the ETV sample introduction methods in micro plasma spectrometry were studied for the plasma formed in glass or quartz chip or tube. No report for atomic emission using ETV in polymer or plastic microchip plasma exists so far. For the PDMS microchip plasma, only gas samples, such as fluorinated carbons, were demonstrated in our previous work.[10] In that report, the background emission spectrum consists mainly of various molecular bands, particularly OH, NH and NO bands and CF_4 gas at 0.1% in argon yields mainly C_2 emission bands. It would be interesting to observe atomic emission in the polymer microchip plasma, which generally requires higher energy than the molecular emission. For the PDMS microchip plasma as an atomization source, it will be useful to introduce aqueous sample to observe atomic or ionic emission.

In this work, a lab-made electrothermal vaporizer (ETV) with tantalum coil[19] is connected to the PDMS polymer microchip plasma to observe atomic emission in aqueous sample. The electrode geometry is changed from top-bottom to side-type for better stability and easy monitoring of emission. Since the plasma is formed inside the PDMS polymer channel, it is interesting to estimate the gas temperature of the plasma as an atomization source, which can be estimated from the OH band emission. For analytical application the atomic emissions of several metals, such as K, Pb, etc, are observed. The analytical figures of merits are determined after optimizing the PDMS polymer microchip-optical emission system with ETV.

Experimental

The schematic diagram of the system used in this experiment is shown in Figure 1.

The rf plasma formed in PDMS polymer to detect fluorinated carbons was described in the previous paper.[10] The electrode geometry of that PDMS polymer microchip plasma was top-bottom type, of which two flat copper electrodes were inserted into the top and bottom slots of the channel, so the electrodes covered the plasma from the top. In this work, the electrode geometry is changed from top-bottom to side-type (L-type) for better stability and easy monitoring of emission, as seen in Figure 2. The electrodes and the torch are molded using PDMS. The plasma torch channel is 2 mm in diameter and 50 mm in length. The top and bottom halves

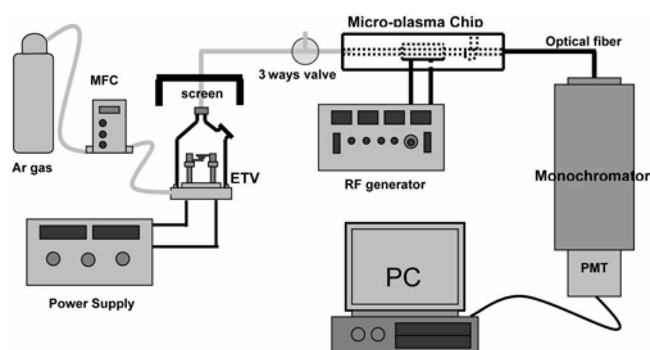

Figure 1. Schematic diagram of ETV-microchip plasma (ETV-MCP) system.

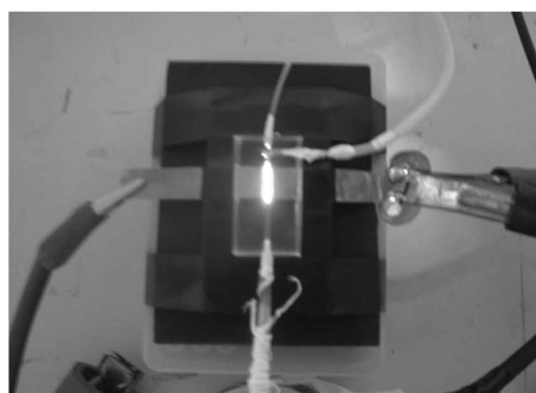

Figure 2. Picture of PDMS polymer microchip plasma with L-type electrode.

of the chip are sealed together by the plasma bonding technique, in which the polymer surface is plasma-treated in the presence of oxygen. An optical fiber for light collection is inserted into the downstream end of the channel. Emission was observed axially using a 0.75 m focal length monochromator (DongWoo Scientific Co. Seoul, Korea) with a grating of 2400 grooves/mm and 80 μm slit widths and a photomultiplier tube (PMT, R950, Hamamatsu Co.). The spectrum was obtained using the software provided by the manufacturer. A purge gas of 300 mL/min flow rate is added to cut off the tail plume of the plasma about 4.5 mm away from the copper electrodes in order to protect the optical fiber. Two flat copper plates (6 mm wide × 0.3 mm thick) are used for the L-type electrodes, so the plasma formed inside the channel can be seen easily from the top. The gap between the electrodes and channel is about 0.5 mm. RF power (27.12 MHz, RF generator and matching box, Model YSE-06F, Youngsin Engineering, Korea) is applied to the electrodes to generate the plasma. The plasma was operated at an rf power of 30-70 W using argon gas at about 300 mL/min regulated by mass flow controllers (MFC, Model 580E series, Brooks, Japan).

Electrothermal vaporization system. For sample solution introduction, the same lab-made electrothermal vaporization (ETV) system reported previously was used,[15] in which the chamber was made of a Teflon base (5 cm × 5 cm × 2.5 cm) and a conical Pyrex glass housing (5 cm in height). The electrodes were made of two copper bars. Tantalum foil (Aldrich, USA), 0.025 mm in thickness and 0.2 Ω in resistance (30 mm × 0.7 mm) for filament was used to vaporize the sample. In routine operation process, a sample of 10-20 μL was loaded onto the tantalum filament and vaporized by thermal energy at 200 °C. After the solvent droplets were vented out through the 3-way valve, the gas flew into the microchip torch, and then, the plasma was turned on for emission measurement. If the sample wasn't dried completely, the plasma can't be turned on. All experimental conditions were the same as the reported before.[19]

The typical electrothermal vaporization system was composed of three parts: a chamber with an argon gas inlet and a sample-injection port, filament and electrodes with a cooling system, and power supply to heat the plate. The chamber was made of a Teflon base and a Pyrex glass housing in a cone shape. The size of the base was 7 cm × 7 cm × 3 cm and the housing was 5.0 cm in base and 7 cm in height. The gas flow of argon inside the housing was in a spiral formation, making the housing cool and efficiently sweeping the vaporized sample into the plasma. The flow rate determined the gas flow rate of the plasma formed in the torch. The electrodes were made of copper bars to give low resistance and high thermal conductivity for cooling. For the filament, a tantalum foil (Aldrich, USA), 0.025 mm in thickness and 0.2 Ω in resistance (30 mm × 0.7 mm) was used to vaporize the sample. The current was supplied to the filament by a power supply (HS-10100D, Max.100A, HwaSung Electronics Corp. Seoul, Korea). The outlet of the chamber was connected to the inlet of the sample injector of the plasma torch through tygon tubing. In order to measure the temperature of ETV gas, a thermocouple detector (AT-3-K, Max 1500 °C, Hanyoung Corp., Seoul, Korea) was used.

Results and Discussion

Plasma formation and ETV system. The plasma formed in a PDMS polymer microchip was stable for more than 8 hrs of operation, and the microchip could be used more than a month. The stability of the plasma strongly depended upon the operating conditions such as the gas flow rates for the plasma formation and cutting gas, the power, and the gap between electrodes. For example, if the flow rate of the cutting gas didn't match with optimum condition, the plasma couldn't be sustained. The plasma condition could be observed from the top because the electrodes were positioned at the side of the channel, so adjustment of the operating conditions can be easily done. If the power was increased to > 90 W, a brighter plasma was observed, but the microchip changed from transparent to yellow. However, this effect didn't reduce the transmittance of the emission into the optical fiber because there was no PDMS between the plasma and the fiber tip. The cutting gas kept the optical fiber from etching.

Optimization of ETV-microchip plasma system. The temperature of the ETV was increased in two steps. First, the solvent, water, was evaporated, and then the dried salts were

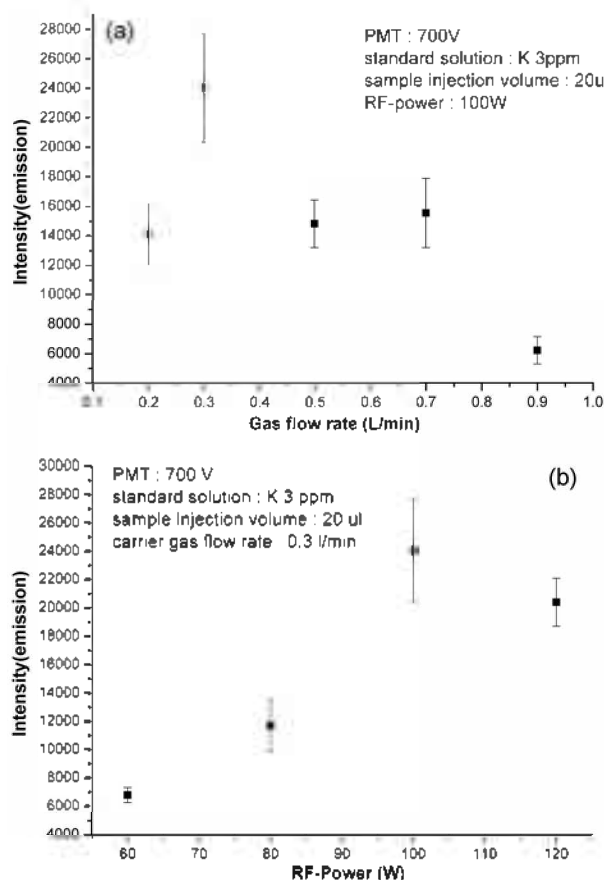

Figure 3. Effect of gas flow rate (a) and rf power (b) on K I intensity in ETV-MCP system.

evaporated. A three-way tee was used to vent the evaporated solvent during the first step prior to introducing analyte particles into the plasma, as shown in Figure 1. Otherwise, the plasma couldn't be sustained. Using this technique, only dry particles were introduced into the plasma.

Gas flow rate and rf power were adjusted for optimization when 3 μg/mL of K was injected. Figure 3(a) shows the signal change of K at 766.49 nm while gas flow rate is varied. The error bars were calculated from data from three different days. Although it could be difficult to find the optimum flow rate, maximum signal was obtained at flow rates between 300-400 mL/min. If the flow rate was over 1.0 L/min, ignition and sustaining the plasma became difficult, and if it was lower than 0.1 L/min, the PDMS microchip was damaged. In this experiment, the cutting gas should be used all the time. The rf power also affected signal intensity of K, as shown in Figure 3(b). At power less than 70 W, the plasma was stable although the intensity was relatively low. As the power was increased, the intensity was increased and maximized at 100 W; however the plasma became unstable. If the power was over 120 W, the PDMS microchip degraded, turning yellow. Clearly, the plasma stability and sensitivity were very dependent on gas flow rate and rf power.

Plasma temperature. Rotational temperature was measured from the diatomic spectrum of OH. The molecular emission intensity was strong enough to be measured even

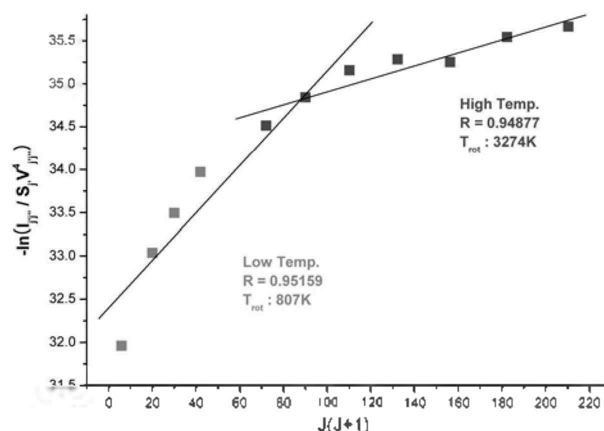

Figure 4. Plot for gas kinetic temperature measurement using OH spectrum.

though no water was introduced. The entrainment of air through the porous PDMS was a likely reason for this. The temperature was calculated using a previously described method.[20] Measurements were made on lines spanning $Q_1(2)$ to $Q_1(14)$ in the 3075-3115 Å region for the OH radical. Several lines were omitted from the calculation because of unresolved bands and spectral interferences. Plotting -ln $(I_{J',J''}/S_{J'}\ \nu_{J',J''})$ against the corresponding excitation energy gave two straight lines with slope equal to 1/kT. A representative plot is illustrated in Figure 4, showing two rotational temperatures, 'low' and 'high'. The low temperature was obtained using the lines of J' value from 2 to 10, and the high temperature was obtained using J' from 8 to 14. This kind of a non-linear rotational distribution was already reported and discussed by several researchers[20] and was characterized as the sum of two separate Boltzmann distributions. and was characterized as the sum of two separate Boltzmann distributions.

As shown in Figure 4, the gas kinetic temperatures were found to be 810 K and 3300 K for the low and the high temperature, respectively. Compared to the low pressure plasma operated at ~1 torr,[20] the low temperature was almost

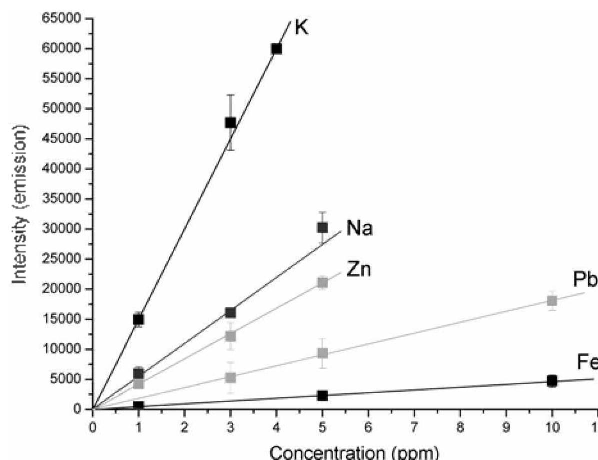

Figure 5. Normalized calibration curves including error bars for K, Na, Pb, Zn, and Fe.

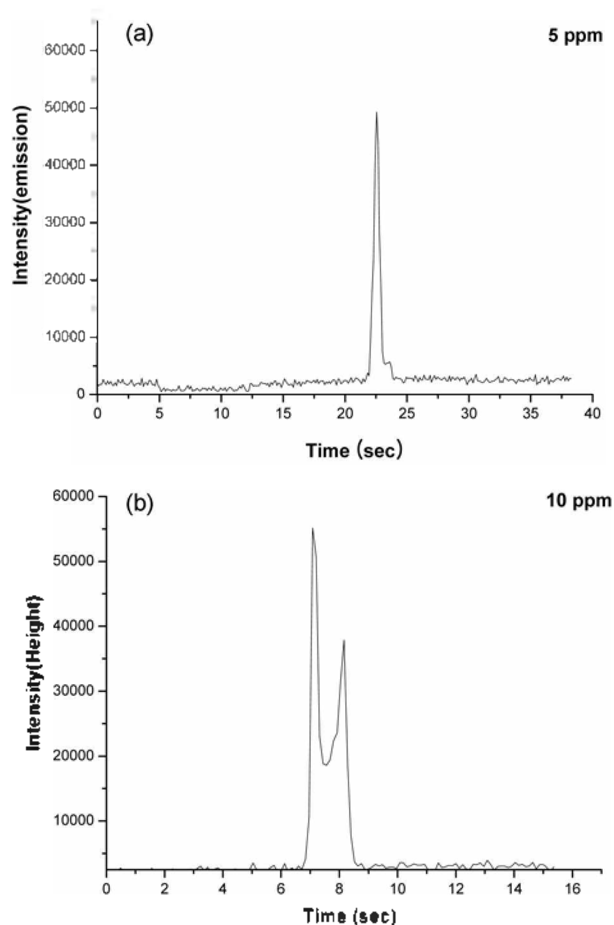

Figure 6. Time resolved spectra of 5 μg/mL K (a) and 10 μg/mL Pb (b) in ETV-MCP system.

the same, and the high temperature was increased. Both temperatures were lower than the results reported for atmospheric pressure plasmas.

Analytical figures of merit. Limits of detection for K, Pb, Zn, Fe, and Na were estimated from the calibration curves. The calibration curves ($R^2 > 0.991$) were obtained from the atomic emission lines of K I, 766.49 nm, Pb I, 405.78 nm, Zn I, 330.26 nm, Fe I, 357.01 nm, and Na I, 588.89 nm. Normalized calibration curves, including error bars obtained by four measurements, are shown in Figure 5. Time resolved spectra of 5 μg/mL K and 10 μg/mL Pb are shown in Figure 6(a) and (b), respectively. Compared to K, the spectrum of Pb had two peaks due to fractionation caused by different anions of the salt. Therefore, integrated peak area was used for the calibration. No ionic emission lines were used for this study due to extremely low emission intensity or no observation. Measurement was repeated four times. Limits of detection of 7 ng/mL, 23 ng/mL, 49 ng/mL, 143 ng/mL, and 597 ng/mL with relative standard deviation of < 5.6% were obtained for K, Na, Zn, Pb, and Fe, respectively, when 10 μL samples in 0.1% nitric acid were injected into the ETV. Based on these results, hybridization of ETV with a PDMS microchip plasma with low rf power made it possible to determine metals in aqueous samples by the observation of atomic lines.

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