High-Power Microwave-Induced Helium Plasma at Atmospheric Pressure for Trace Element Analysis

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Keywords: atmospheric pressure plasma, microwave-induced plasma, trace element analysis, atomic emission spectrometry, detection limit, excitation temperature, Okamoto cavity

The detection of lower levels of non-metals (e.g., F, Cl, Br, S, P, C etc.) in aqueous solutions is of great environmental and material importance. However, the determination of the non-metals by atomic emission spectrometry (AES) has been quite limited, because the emission lines for the non-metals are the higher excitation potential in comparison with most other elements. For example, the detection of fluoride by AES is proven particularly difficult. The resonance line for fluoride appears at 95.5 nm. Consequently, the work with fluoride has utilized non-resonance lines, particularly the F I (685.6 nm). A helium (He) plasma is better suited for the determination of non-metals, because He has the highest ionization potential.

High-power (~ 1,000 watt CW, 2.45 GHz) annular-shaped helium microwave-induced plasma (He-MIP) at atmospheric pressure was generated by the Okamoto cavity. A schematic diagram of the experimental system is shown in Fig.1. The Okamoto cavity is a non-resonant cavity without cooling and consists of two parts. One section is a flat rectangular waveguide with a reduced height (electric field plane: 6.0 mm) for impedance matching between the resultant impedance of the cavity and that of the He plasma in order for the plasma to absorb the power efficiently. The other section is a mode transformer which consists of an inner conductor (i.d.: 16 mm) and outer cylindrical conductor (i.d.: 40 mm) terminated by a front plate. The ring-gap distance between the front plate and the front edge of the inner conductor is 5 mm. The azimuthal symmetric surface wave is excited in the ring-gap and is coupled to the discharge tube (quartz) placed inside the cavity. Then the annular He plasma was generated in the discharge tube and run with 300 ~ 1,000 watt (power source limit) of forward microwave power and zero reflected power after tuning with a three-stub tuner. The torch (discharge tube) used was a tangential flow torch made of quartz. The torch (10 mm o.d., 8 mm i.d.) consists of two concentric tubes, as well as two gas flows. A central carrier-gas flow for sample introduction and a outer plasma-support-gas flow with a spiral trajectory, for plasma support, were used. The gas used is helium (purity: 99.995 %). The inner tube is turp-shaped and the gap between the two concentric tubes is 0.3 mm which affect the production of annular plasma. An aqueous nonmetal solution was injected into the plasma by an ultrasonic system with desolvation and condensation.

The monochromator (Ebertt type) has a focal length of 1 m and was equipped with a 1200 lines/mm grating was used. The detector was photomultiplier tube (Hamamatsu, R955). The signal from the tube was converted to a voltage and analog voltage was digitized and analog-to-digital converter, and processed by a computer.

The electron density and iron-excitation temperature of the plasma were measured using the Stark broadening of H β (486.1 nm) and the Boltzmann plot method using an aqueous Fe as the thermometric species, respectively. Electron density and the temperature on the order of 10^{14}/cm^3 and 6,500 K were measured, respectively. Intense atomic emissions were detected and the detection limit of 100 ppb for F I (685.6 nm), 100 ppb for Cl II (479.6 nm), 150 ppb for Br II (487.5 nm), 1 ppb for C I (247.9), 2 ppb for P I (213.6 nm), 0.02 ppb for Mg II (279.6 nm) and 0.02 ppb for Ca II (393.4 nm) were obtained. The detection limit was calculated as the concentration of the analyte that gives a signal equal to three times the standard deviation of the background noise of the blank solution (% HNO₃).
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An annular helium plasma at atmospheric pressure was generated by the 2.45 GHz microwave power (~ 1 kW) with Okamoto cavity, and the physical and analytical characteristics were summarized. The electron density and iron excitation temperature of high energy part for the He plasma were on the order of $10^{14}/\text{cm}^3$ and 6,500 K, respectively. An aqueous solution with non-metal was injected into the plasma by the ultrasonic system with desolvation and condensation. Intense atomic and/or ionic emissions were detected and the detection limit of 100 ppb for F I (685.6 nm), 100 ppb for Cl II (479.5 nm), 150 ppb for Br II (487.5 nm), 1 ppb for C I (247.9 nm), 2 ppb for P I (213.6 nm) and 0.02 ppb for Mg II (279.6 nm) and Ca II (393.4 nm) were obtained.

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1. Introduction

Increasing environmental pollution involving water resources, air and soils has created the necessary for precise monitoring of pollutants in rivers, woodlands and agricultural grounds over large areas(1). Especially, the detection of increasing lower levels of nonmetals (e.g. F, Cl, Br, I, C, P, etc.) in aqueous solutions is of great environmental and material importance.

A helium (He) plasma is better suited for the determination of nonmetals, because He has the highest ionization potential(1). However, existing inductively-coupled He plasma (He-ICP) is the lower efficiency and the higher detection limits(1). While, the microwave-induced He plasmas (He-MIP), Beenakker cavity, sufatron and microwave plasma torch (MPT), have low tolerance to aqueous solution samples, because the input microwave power is limited up to 500 watt(1). The low-power MIP does not provide sufficient plasma energy to both desolvate and ionize the elemental mass from the directly nebulized sample solution. Recently, the Kilowatt-plus-MIP (Kip-MIP) and capacitively coupled microwave plasma (CMP) with high power (Kip-MIP: 1,600 watt and CMP: ~ 1,000 watt) were developed. However, the detection limits of these plasmas were high, for example, He Kip-MIP, Cl II (479.5 nm): 2.2 ppm (µg/ml)(2), because these plasmas are the low temperature and without an annular-shape.

We have generated the high-power (~ 1,000 watt CW, 2.45 GHz) annular-shaped N₂, O₂, Air, Ar and He-MIPs by an Okamoto cavity(3)(8) and the detection limits of 0.1 ppb for F I (685.6 nm) and Cl II (479.5 nm) were obtained by the He-MIP(7)(9).

In the present work, the physical and analytical characteristics such as the excitation temperature and the detection limits of the He-MIP produced by the Okamoto cavity will be described.

2. Experimental

A schematic diagram of the experimental system is shown in Fig.1(1). The Okamoto cavity is a non-resonant cavity without cooling and consists of two parts(4). One section is a flat rectangular waveguide with a reduced height (electric field plane; 6 mm) for impedance matching between the resultant impedance of the cavity and that of the He plasma in order to absorb the power for plasma efficiently. The other section is a mode transformer which consists of an inner conductor (i.d.: 16 mm) and outer cylindrical conductor (i.d.: 40 mm) terminated by a front plate. The ring-gap distance between the front plate and the front edge of the inner conductor is 5 mm. The axial symmetric surface wave is excited in the ring-gap and is coupled to the discharge tube (quartz) placed inside the cavity. Then the annular He plasma was generated in the discharge tube and run with 300 ~ 1,000 watt (power source limit) of forward microwave power and zero reflected power after tuning with a three-stub tuner (He-MIP).

The torch (discharge tube : 10 mm o.d., 8 mm i.d.) with tangential flow made of quartz and consists of two concentric tubes, as well as two gas flows. A central carrier-gas flow for sample introduction and a outer plasma-support-gas flow with a spiral trajectory, for plasma support, were used. These flow rates are referred to as Gc and Gp, respectively. The gas used is helium (purity: 99.995 %). The inner tube is tulip-shaped and the gap between the two concentric tubes is 0.3 mm which affects the production of annular-shaped plasma and the value of Gp.

An aqueous solution sample (NaF, NaCl, KBr, Fe, C, or P : 1,000 ppm (µg/ml), or Mg or Ca: 10 ppm in 5 % HNO₃ solution) was introduced into the He plasma using an ultrasonic nebulizer with a desolvation and condensation system (Cetac:U-5000 AT) and a peristaltic pump. During sample introduction, the mist produced by the transducer was carried by He flow through a heating tube (desolvation, 150 °C) and condenser (~ 2 °C) which were used for droplet desolvation and condensation, respectively. The sample aerosol was introduced into the center of the annular He plasma through the inner tube along with the carrier-gas.
The measuring instrument used in this work has been described previously (6). The monochromator (Ebert type) has a focal length of 1 m and was equipped with a 1200 lines/mm grating. The detector was a photomultiplier tube (Hamamatsu, R955). The signal from the tube was converted to a voltage and analog voltage was digitized an analog-to-digital converter, and processed by a computer.

The He plasma was observed in an “end-on” mode where the axis of the plasma was perpendicular to the slit of the monochromator or “side-on” mode where the axis of the plasma was parallel to the slit.

3. Results & Discussion

3.1 Production of He-MIP

Figure 2 shows the photograph of the He-MIP at atmospheric pressure with aqueous NaF solution nebulization. The stable region of the annular He, Ar, O2 and N2 plasma production are shown in Fig.3. Where, the carrier gas flow rate Gc is 0.2 l/min. By increasing the microwave power, the lower limit of Gp shifts to higher values in order to confine the plasma and cool the discharge tube. This is due to the fact that the plasma pressure (product of electron density and temperature) and the plasma diameter increase with increasing the microwave power.

Figure 4 shows the axial emission intensity distribution of He I (587.6 nm, upper level energy : $E_u = 23.07$ eV) and N2 II (391.4 nm, $E_u = 15.5$ eV) as a parameter of microwave power. Here, the plasma was observed in a “side-on” mode. The latter line is due to the ionization of ambient air. The high energy and the longer tail flame plasma is expected to have longer analytical residence time of analytes in the plasma.

3.2 Electron Density & Temperature

Electron density and the excitation temperature of He plasma were measured using the Stark broadening of Hβ (486.1 nm) (38) from the sample solution (see Fig.6) and the Boltzmann plot method using aqueous Fe as the thermometric species (1)(6), respectively. The Stark full-width at half maximum $\Delta \lambda$ and the electron density $N_e$ [cm$^{-3}$] are related by $N_e = \{\epsilon(2.50 \times 10^9\alpha)\}^{3/2}$, where $\alpha$ is the half-width parameter ($7.87 \times 10^{-3}$) (38). The excitation temperature was calculated from the Boltzmann plot of log($I_\lambda$/$g_f$) vs. $E_u$, giving a slope equal to $-0.434 \, kT$, where $I_\lambda$ is the emission intensity of the line (arb. units), $\lambda$ is the wavelength (nm), $g$ is the statistical weight of the upper state, $f$ is the oscillator strength, $E_u$ is the energy of the upper state in the transition (cm$^{-1}$), $k$ is the Boltzmann constant and $T$ is the excitation temperature (K) (1)(6).

Here, nine iron lines (372.0, 372.3, 372.7, 373.5, 373.7, 374.6, 375.0, 375.8 and 381.6 nm) were used. The Boltzmann plot for these lines yields not a single straight line as shown in Fig.5. The
The high energy component of the line slope is 6,500 K and the low one is 3,500 K. As shown in Fig. 5, in the case of a single line for these lines is 5,000 K. Under the same experimental conditions, the electron density was $2.1 \times 10^{14}/\text{cm}^3$. The electron density is higher than that reported for a He-ICP ($5 \times 10^{13}/\text{cm}^3$) but similar to that for the He-CMP ($4 \times 10^{14}/\text{cm}^3$). However, the temperature is higher than that reported for He-CMP (3,400 K) and He-ICP (4,300 K). These results are summarized with other plasmas in Table 1.

![Height From Front Plate (mm)](image1)

**Fig. 4.** Axial emission intensity distribution of He (I) and N\textsubscript{2} (II) as a parameter of microwave power

![Log I (2\textsuperscript{a}g)](image2)

**Fig. 5.** Boltzmann plot for Fe (I) upper levels with He-MIP; Microwave power = 600 watt, $G_p = 10 \text{ l/min, } G_c = 0.3 \text{ l/min}$

**Table 1.** Comparison of electron density and excitation temperature (Fe) for various plasmas

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<tr>
<td>Electron Density (cm\textsuperscript{-3})</td>
<td>$2.1 \times 10^{14}$</td>
<td>$5 \times 10^{13}$</td>
<td>$5 \times 10^{13}$</td>
<td>$1.2 \times 10^{14}$</td>
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<tr>
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* used Okamoto cavity

![Spectrum](image3)

**Fig. 6.** Spectrum obtained nebulizing a NaCl + KBr (250 ppm) into the He-MIP. Microwave power = 500 watt, $G_p=10 \text{ l/min, } G_c=0.3 \text{ l/min}$
3.3 Analytical Characteristics

The detection of halogens by atomic emission spectrometry has been quite limited, because the resonance lines for the halogen are in the vacuum ultra violet region (bromide Br: 154.1 nm, chloride Cl: 134.7 nm, and fluoride F: 97.8 nm) and the higher excitation potential in comparison with most other elements; the upper excitation potential of the line is more than 10 eV. However, using the He-MIP which has the high energy electrons, the halogen can be detected using the non-resonance lines: Br II (470.5 nm, $E_u = 14.2$ eV), Cl II (479.5 nm, $E_u = 15.9$ eV) and F I (685.6 nm, $E_u = 14.5$ eV). A typical Br and Cl emission spectrum for the He-MIP is shown in Fig.6. Here, the microwave power is 500 watt, and Gp and Ge are 10 l/min and 0.3 l/min, respectively. As can be seen in Fig.6, He I (471.3 nm, $E_u = 23.7$ eV) and He II (486.1 nm, $E_u = 12.8$ eV) lines from the plasma gas and the sample solution were also obtained. With increasing the microwave power, these emission intensities increased sharply at first and then saturated.

The detection limit was calculated as the concentration of the analyte that gives a signal equal three times the standard deviation of the background noise of the blank solution (5% HNO3) ($3\sigma$). The detection limit of 100 ppb for F I (685.6 nm) was obtained. Table 2 shows the detection limits for other elements and compared with other systems. The present system produced much better detection limit than other systems. This is due to the fact that the present He-MIP has the high energy electrons and the annular-shape, and the sample is efficiently ionized in the center of the plasma.

### Table 2. Comparison of detection limits (ppb)

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<td>Br(II)</td>
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<td>150</td>
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<td>F(I)</td>
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<tr>
<td>Mg(II)</td>
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<tr>
<td>Ca(II)</td>
<td>391.4</td>
<td>3.2</td>
<td>0.02</td>
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4. Conclusion

Characteristics of a simple high-power helium microwave-induced plasma (He-MIP) at atmospheric pressure generated by the Okamoto cavity for trace element in an aqueous solution was presented and it was clear that the He-MIP is a useful for non-metal detection. An excitation temperature for high energy electrons of about 6,500 K and an electron density in the $10^{14}/cm^3$ range were obtained at 600 watt input microwave power.

Then the detection limit of 100 ppb for F I (685.6 nm), 100 ppb for Cl II (479.5 nm), 150 ppb for Br II (487.5 nm), 1ppb for C I (247.9 nm), 2 ppb for P I (213.6 nm) and 0.02 ppb for Mg II (279.6 nm) and Ca II (393.4 nm) were obtained.

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References

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