Langmuir Probe Potential Measurements for Reduced-pressure Inductively Coupled Plasma Mass Spectrometry

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A floating Langmuir probe was used to measure the apparent dc offset potential of a reduced-pressure inductively coupled plasma near a substitute sampling orifice of a mass spectrometer. The experimental results demonstrate that the dc offset potential causes the secondary discharge at the sampling orifice. The plasma potential is in the range +3.5 to +20 V and varies with the plasma operating conditions. The manner by which a water-cooled torch is shielded has a substantial effect on the plasma potential, then the secondary discharge. The measured values of the potential give a good explanation for the enhanced capacitive coupling effect in reduced-pressure ICP-MS reported previously.

Keywords: Reduced-pressure plasma; inductively coupled plasma mass spectrometry; plasma potential; secondary discharge; Langmuir probe

Recently, a number of investigations on reduced-pressure inductively coupled plasma mass spectrometry (ICP-MS)†–4 have shown its potential in solving the problems encountered in conventional atmospheric pressure ICP-MS, such as numerous polyatomic interferences, ionization difficulties for non-metals and high gas and power consumption. Evans and Caruso2 reported easy plasma generation for a number of gases, such as He, O₂, N₂ and air. The detection limits obtained for halogenated gas chromatographic eluents using a helium low-pressure ICP-MS system are comparable to those found with helium MIP-MS.3 The capability of adjusting the degree of fragmentation of organic components was also demonstrated with the employment of very low incident power (15–50 W).4 In our fundamental study on the characteristics of reduced-pressure ICP-MS,1 it was found that the ionization efficiency of non-metallic elements could be much improved owing to the obvious deviation from local thermal equilibrium (LTE) and the energy transfer from high kinetic energy electrons. This was confirmed later through alkali metal halide determination using tungsten filament high-capacity condenser discharge ETV as a quantitative sample introduction method.5

With the same sustaining plasma gas of argon, order of magnitude lower detection limits for Cl and Br were achieved at reduced pressure (17 Torr) compared with those obtained at atmospheric pressure. Among the cases cited above, plasma gas consumption was reduced to a very low level.

As shown previously,5 a lower coolant gas flow rate (e.g., 50 ml min⁻¹) is to be preferred for non-metallic element analysis, while keeping the forward power as high as possible (e.g., 500 W). Therefore, an efficient water cooling system is needed for the reduced pressure ICP torch to avoid overheating. However, the presence of water between the load coil and the plasma would enhance the capacitive coupling effect of radio-frequency (rf) power with the plasma and result in a violent secondary discharge at the sampling orifice.6 This phenomenon was particularly serious at lower pressure, where strong copper signals originating from the sputtering of the sampling orifice were observed in mass spectra.1 Further investigation showed that the employment of an electrostatically shielded water-cooled (ESWC) torch configuration could be an effective way to eliminate the secondary discharge, and the capacitive coupling effect can be controlled by a carbon-film resistor inserted in the shielding circuit.7

Generally, it is recognized that the secondary discharge occurring at the sampling orifice is correlated with the rf and then the dc plasma potential originating from the capacitive coupling effect.1–6 Therefore, a higher dc offset potential could be assumed for reduced-pressure ICP-MS, especially at low pressure. Usually, the plasma potential can be estimated directly with a Langmuir probe measurement8–10 or indirectly via ion kinetic energy determination.8 It should be noted that, since the mobility of electrons in the plasma is much higher than that of positive ions, electrons will movepreferentially to the probe, leaving a positively charged plasma. This process continues until the potential between the plasma and probe is sufficient to keep the plasma neutral. Under this condition, the probe is at floating potential. The plasma potential is always slightly positive with respect to the floating potential (plasma-sheath property). In reality, the floating potential is the quantity that is being measured. However, the Langmuir probe can provide useful information, although approximate, about the ICP potential, because the error introduced is less than 1 V,8,11 which is much lower than the plasma potential reported in the literature.9–10 Hence the floating potential is taken as the plasma potential in the present paper.

Here, a special Pyrex discharge chamber was constructed to be incorporated with the original extended torch used for reduced-pressure ICP-MS.1–5 The dc offset plasma potential was measured by a floating Langmuir probe inserted into the reduced-pressure ICP and the effects of plasma parameters (e.g., power, pressure and gas flow rate) and the shielding plate grounding mode are discussed.

EXPERIMENTAL

Discharge Chamber

The details of the plasma potential measurement system for reduced-pressure ICP-MS are shown in Fig 1; additional information about the ICP generator, matching box and extended ESWC torch can be found in a previous paper.1 For the convenience of inserting the Langmuir probe into the plasma, the mass spectrometer sampling interface was replaced with a specially designed Pyrex interface chamber (Glass Machine Shop, University of Nagoya, Nagoya, Japan).

Because the dc offset potential of the plasma was thought to originate from the contact of the ICP with the grounded...
Fig. 1 Schematic diagram of the plasma potential measurement system for reduced-pressure ICP-MS.

sampling cone, a substitute sampling cone was fixed inside the interface chamber at the same distance from the load coil as the original sampling cone (17 mm). The substitute sampling cone was constructed from a 10 mm thick copper plate with a 1.0 mm diameter central hole drilled through it; the front of the hole can be used to observe the secondary discharge approximating the real one with the original sampling cone. The substitute sampling cone was grounded through a 1.0 mm diameter copper rod inserted into the central hole from the end side. In order to make the most of the pumping efficiency, six 5 mm diameter holes were drilled around the fringe of the sampling cone. It could be noted that for convenience of chamber fabrication and experimental manipulation, the 10 mm thick flat plate is different from the thin, pointed, sampling cone in MS. The vacuum system is also slightly different, which may result in different flow rates to those under normal MS conditions. Although the absolute values may not reflect the actual MS interface, measurements were carried out to investigate the trend of the plasma potential with variations in plasma conditions, which may help us explore in more detail the secondary discharge occurring in reduced-pressure ICP-MS.

As shown in Fig. 1, the Pyrex interface chamber was water cooled. The end tube of the chamber was stopped by a silicone-rubber septum through which the copper rod lead wire protruded for grounding. The side tube was connected to a rotary vacuum pump (372 l min$^{-1}$). A Varian vacuum valve (4 mm id) was inserted into the vacuum line before the rotary pump; thus the pumping speed of this system could be adjusted over a wide range. The vacuum gauge was the same as used previously.

**Langmuir Probe**

The Langmuir probe consists of a tungsten wire (0.4 mm diameter) sealed into a demountable tapered Pyrex plug. This plug is fitted in a socket opened on the wall of the interface chamber. The plug and the socket are ground fit and can be sealed by vacuum grease. The plug containing the probe can be changed very easily if needed. The tip of the tungsten wire rod is sheathed with an alumina sleeve so that only a short length of 1 mm is exposed to the plasma. External cooling of the probe is unnecessary because of the comparatively lower forward power (usually 300 W) and lower gas flow rate. The argon environment also prevents the tungsten probe from forming an appreciable oxide coating. Very little etching of the probe has been observed over extended periods of use.

To investigate the cause of the secondary discharge, the position of the probe tip was set right in front of the sampling orifice and the measuring procedure was similar to that reported previously. The rf wave picked up by the probe was monitored with an oscilloscope (Iwatsu SS-5711D, 50 MHz) through a 10:1 signal attenuator. The peak-to-peak ($V_{pp}$) and dc offset ($V_{dc}$) voltages of the rf wave were measured from the oscilloscope traces. $V_{av}$, i.e., the arithmetic mean of the positive and negative peak voltages, is considered to be the plasma potential and it is positively biased normally. Because the ICP is in contact with the grounded sampler, when the plasma potential is driven positive, ions attempt to reduce the potential by carrying current to the sampler. A rectification effect occurs, and the average plasma dc potential usually becomes positive with respect to the ground.

In order to examine the interference from the ICP’s high rf power environment when using a Langmuir probe, a 100–500 W rf power was applied to the load coil without igniting the plasma. The peak-to-peak rf voltages picked up by the probe were less than 1 V and the averaged dc potentials were barely measurable, which suggests that the potential picked up by the probe was all due to the plasma potential itself and the contribution from the induction effect of the probe can be ignored.

**Reagent**

Ultra-high purity argon gas (99.9995%) served as the plasma gas to reduce the interference from gas species under the plasma conditions.

**RESULTS AND DISCUSSION**

**General Observations**

The assembly shown in Fig. 1 permits a stable ICP to be sustained at a power level between 30 and 800 W and plasma gas flow rates from less than 1 ml min$^{-1}$ to several liters per minute. The ease of plasma generation at reduced pressure and self-ignited phenomena were confirmed again when the pressure was lower than 10 Torr.

As the interface chamber is made of glass, the appearance
of the reduced-pressure ICP can be clearly observed. It was found that the shape and color of the plasma varied with the change of pressure and incident power. At a low pressure (several Torr), the ICP was diffuse, with its tail reaching about 10 mm behind the substitute sampling cone with a bluish to purplish color. On the other hand, when the plasma was generated under higher pressure and forward power, its appearance resembled an atmospheric pressure ICP, condensed and whitish. However, the inner gas flow can always punch the plasma, leaving a clearly discernible 'donut' structure. Usually, a higher gas flow rate requires a corresponding higher forward power to support. Judging from the appearance of the tungsten probe surface, it seems that the gas temperature increased with increase in pressure while keeping the forward power constant.

Another important phenomenon pertinent to the present experiments was that when the sampling cone was grounded through the copper lead wire, an obvious discharge could be observed in the vicinity of the central hole at low pressure. However, this discharge disappeared as soon as the lead wire became floating. Simultaneous plasma potential measurement indicated that if the sampling cone was kept floating, the average dc offset potential always equaled zero, although the peak-to-peak potential varied with the plasma operating conditions. The above results confirm and clarify that the dc offset potential originates from the existence of the grounded sampling cone and it is this dc offset potential which causes the secondary discharge.  

**Effect of Forward Power**

The dependences of the dc offset voltages ($V_{av}$) measured at 7.5 and 17 Torr on the rf forward power are presented in Fig. 2(a) and (b), respectively, for different torch shielding modes. It can be seen from Fig. 2 that $V_{av}$ varies from several volts to 20 V and is identical with what has been reported for atmospheric pressure ICP-MS, although considerably lower power was used here.

Apparently, $V_{av}$ continues to increase with increase in forward power in any case. This can be explained by the enhanced capacitive coupling between the load coil and the plasma with increase in rf power and, generally, a higher $V_{av}$ corresponds to a higher $V_{pp}$.

At the same forward power, $V_{av}$ is highest with the WC torch and lowest with the grounded ESWC torch over the whole range of rf power examined. The grounding mode of the shielding plate plays an important role in the dc offset potential. ESWC.G or even ESWC.10Ω can reduce $V_{av}$, and thus the secondary discharge, efficiently, which gives a good explanation for the phenomena reported previously.

**Effect of the Shielding Circuit Resistance**

It has been reported previously that the capacitive coupling effect of rf power between the load coil and the plasma can be controlled by the adjustment of the shielding circuit resistance. Here, the dc offset potentials were measured by inserting 10, 20 and 100 Ω carbon-film resistors into the shielding circuit with the other operating parameters (20 Torr, 300 W) maintained the same as before. The results are shown in Fig. 3, and the variation of the copper ion signal ($^{63}\text{Cu}^+$) obtained previously is also shown for comparison. In Fig. 3, 0 Ω represents the shielding plate being grounded directly, and both $V_{av}$ and the copper ion intensity are normalized to those for the floating mode.

Clearly, the $V_{av}$ tendency tallies with the behavior of $^{63}\text{Cu}^+$. With the decrease in resistance, $V_{av}$ decreases abruptly between 0 (floating) and 20 Ω, then levels out. It should be mentioned that there are still several volts of $V_{av}$ left even though the shielding plate was grounded directly. However, provided that this voltage is close to, or less than, the breakdown value

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**Fig. 2** Variation of $V_{av}$ as a function of the forward power at (a) 7.5 and (b) 17 Torr for different torch shielding modes. The outer, intermediate and carrier gas flow rates are (a) 45, 0 and 15 and (b) 50, 0 and 180 ml min$^{-1}$, respectively. WC, water-cooled torch; ESWC.F, ESWC.G and ESWC.10Ω, the shielding plate of the ESWC torch was floating, grounded or grounded through a 10 Ω resistor, respectively.

**Fig. 3** Variation of $V_{av}$ and $^{63}\text{Cu}^+$ as a function of the resistance between the shielding plate and ground.
needed for the sputtering of sampling cone material, there will be few or no copper ions to be observed. The resistance effect can be explained by the existence of a shielding circuit allowing some part of the rf current to flow to the ground through the shielding plate, which results in a lower rf power coupled to the plasma. Because the shielding circuit resistance affects $V_{av}$ directly, the secondary discharge can be controlled by adjusting the resistance. The similarity between the $V_{av}$ and Cu$^+$ curves confirms again that the dc offset potential of plasma is the main cause of the secondary discharge.

**Effect of Gas Flow Rates**

The effect of gas flow rates on $V_{av}$ was investigated with an ESWC torch, keeping the shielding plate floating. The carrier and outer gas flow rate effects are shown in Fig. 4(a) and (b), respectively, the corresponding pressure values being given adjacent to each point.

As shown in Fig. 4(a), with a change in carrier gas flow rate from 0.2 to 0.8 l min$^{-1}$ while holding the outer gas flow rate (OG) at 0.8 l min$^{-1}$, an increase in plasma pressure from 87 to 130 Torr results in a decrease in $V_{av}$ from 16.5 to 11.5 V. When the outer gas flow rate was lowered to 0.2 l min$^{-1}$, $V_{av}$ also followed the same trend but with a smaller slope. Both curves tally with our previous report that the secondary discharge effect was much more intense at lower pressure.$^1$ However, it should be mentioned that these two curves intersect in the lower carrier gas flow rate region, which suggests that in addition to plasma pressure, $V_{av}$ must be influenced by some other factors at the same time.

Fig. 4(b) shows the dependence of $V_{av}$ on the outer gas flow rate while keeping the carrier gas flow rate (CG) at 0.2 and 0.8 l min$^{-1}$. When the carrier gas flow rate is kept at 0.8 l min$^{-1}$ (lower curve), $V_{av}$ increases with decrease in the outer gas flow rate, because the pressure decreases at the same time. At a carrier gas flow rate of 0.2 l min$^{-1}$ (upper curve), however, $V_{av}$ decreases with decrease in the outer gas flow rate, although very slowly. This indicates again that in addition to the pressure, some other factors exist that affect $V_{av}$.

**Effect of Pressure**

In order to study the effect of the plasma pressure alone on $V_{av}$, the sum of the carrier gas and outer gas flow rates was kept constant (at 0.8+0.2 and 0.2+0.8 l min$^{-1}$), and the pressure was changed by changing the pumping speed with a needle valve. The results are shown in Fig. 5.

As expected, $V_{av}$ increases with decrease in the plasma pressure when holding the gas flow rates constant. This phenomenon might be explained as follows: the mobility difference between the electrons and ions in the plasma was increased with increase in the mean free path at lower pressure, and electrons will move much more preferentially to the probe, leaving a much higher positively charged plasma. However, this pressure effect reminds us that the enhanced ion signals of halogens obtained at reduced pressure in the previous work may partly be contributed to by the intense secondary discharge since a WC torch was used.$^5$ From the two curves in Fig. 5, it can be seen that the increase in the proportion of carrier gas in the total gas flow rate will cause a decrease in $V_{av}$ when the overall gas flow rate is kept constant, which is different from the result reported for atmospheric pressure ICP-MS.$^6,7$ The reason for these results could not be clarified in the present experiments.

**CONCLUSION**

The present work not only demonstrates the feasibility of Langmuir probe measurement of the plasma potential in reduced-pressure ICP-MS but also clarifies some ideas about the secondary discharge. The measured values of $V_{av}$ tally well...
with the intensity of secondary discharge at the sampling orifice, which indicates that $V_{av}$ is the main reason for the discharge. The electrostatically shielded torch configuration can greatly attenuate the secondary discharge via the decrease in $V_{av}$. The positive dc offset potential increases with increase in the forward power and decreases as the plasma pressure increases. The gas flow rate, especially the carrier gas flow rate, also plays an important role in $V_{av}$, and usually a higher flow rate leads to a lower potential.

The authors thank Mr. T. Tanabe of Nagoya University for fabricating the Pyrex discharge chamber and Langmuir probe.

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Paper 6/06934G
Received October 9, 1996
Accepted February 26, 1997