Inductively Coupled Plasma Mass Spectrometry with Low-Power Nitrogen and Oxygen Plasmas

Tomokazu Tanaka, Kazukuni Yonemura, Kentaro Obara and Hiroshi Kawaguchi

Department of Materials Science and Engineering, Nagoya University, Nagoya 464-01, Japan

With a low-power radio-frequency generator (1.8 kW, 27.12 MHz), N\textsubscript{2} and O\textsubscript{2} plasmas were obtained by slightly modifying the load coil and matching circuit. After the Ar plasma was generated, the outer and carrier gases of Ar were gradually replaced by N\textsubscript{2} or O\textsubscript{2}. The replacement of the intermediate Ar gas by N\textsubscript{2} or O\textsubscript{2}, respectively, were comparable or lower for the elements with ionization potentials lower than 6.5 eV, but generally higher for the other elements, compared to those obtained with the Ar plasma. Polyatomic ions resulting from Ar, such as Ar\textsuperscript{O+} and Ar\textsuperscript{2+}, were considerably attenuated with the N\textsubscript{2} and O\textsubscript{2} plasmas, although the intensities of ArN\textsuperscript{+} and analyte oxide ions increased with these plasma, respectively.

Keywords Inductively coupled plasma mass spectrometry, nitrogen plasma, oxygen plasma, spectral interference, low-power radio-frequency generator

Inductively coupled plasma mass spectrometry (ICP-MS) is rapidly becoming popular in various fields as one of the most sensitive techniques for multi-element trace analysis. The spectral interferences resulting from Ar adducts, however, are unavoidable because the ICP is usually generated with Ar gas. Particularly in the m/z range below 80, the spectral overlaps between analyte and poly-atomic ions (e.g., \textsuperscript{56}Fe\textsuperscript{+} and \textsuperscript{40}Ar\textsuperscript{16}O\textsuperscript{+}, and \textsuperscript{78}Se\textsuperscript{+} and \textsuperscript{40}Ar\textsuperscript{2+}Ar\textsuperscript{+}) are becoming a serious problem.

As an approach for the attenuation of poly-atomic ion interferences caused by Ar, the employment of a mixed gas plasma has been investigated.\textsuperscript{1-4} In most of these experiments, the signals of background species relating to Ar could be decreased considerably by the addition of a small amount of N\textsubscript{2} to the outer or carrier gas. Lam and Horlick\textsuperscript{1} showed that the addition of 5% N\textsubscript{2} to the outer gas resulted in a signal enhancement, while Beauchemin and Craig\textsuperscript{2} reported that the sensitivity was reduced by the addition of N\textsubscript{2}. Since there is no general agreement yet on its practical usefulness, the ICP-MS with the mixed-gas plasma should be explored more extensively. Furthermore, there have not been any reports on ICP-MS with the plasma whose gases are completely replaced by molecular gases.

In ICP atomic emission spectrometry (AES), N\textsubscript{2} plasmas have been generated with a high-power (>2 kW) and/or a higher frequency (e.g. 40.68 MHz) generator or by using a torch with a special configuration.\textsuperscript{5} No attempt, however, has been published to generate the N\textsubscript{2} plasma by using a radio-frequency (RF) generator with a power less than 2 kW and a frequency of 27.12 MHz.

In the present study, we attempted to generate the N\textsubscript{2} or O\textsubscript{2} plasma using a low-power RF generator (1.8 kW and 27.12 MHz) and a conventional torch. A slight modification of the load coil and matching circuit enabled us to replace the outer and carrier Ar gases by N\textsubscript{2} or O\textsubscript{2}, but the addition of N\textsubscript{2} into the intermediate Ar gas was impossible. The outer and carrier Ar gases could be more easily replaced by O\textsubscript{2} than by N\textsubscript{2}, and the addition of O\textsubscript{2} into the intermediate Ar gas was possible up to 60% after the complete conversion of the outer and carrier gases into O\textsubscript{2}.

Experimental

Instrumentation

A laboratory constructed ICP mass spectrometer\textsuperscript{6-4} was used, in which the RF generator (27.12 MHz, 2 kW max., Shimadzu Mfg. Co., 2H-S), the matching box with a manual impedance adjustment and the ICP torch (Shimadzu Mfg. Co.) were commercial ones for ICP-AES. Gas regulators with flow meters for N\textsubscript{2} or O\textsubscript{2} were attached in parallel to all of the three flows of Ar; outer, intermediate and carrier gases, to control the flow rates of these gases independently.

A sample solution containing 1 µg/ml each of Co, Y, In, La and Eu, as well as 1% nitric acid, was used for the measurement of mass spectra. Detection limits of elements...
were measured by using standard solutions of the elements of appropriate concentration. In the mass range less than 50 m/z appeared strong peaks of N⁺, N₀⁺ and N₂⁺ for N₂ plasma and O⁺ and O₂⁺ for O₂ plasma in addition to the ion peaks related to Ar and water. Therefore a mass range from 50 to 165 m/z was measured in this experiment. Signal counts with a dwell time of 2 ms were stored in 512-channel memories of a multichannel analyzer and the scanning was repeated 45 times. The peak intensities of analyte and polyatomic ions measured with each plasma were calculated by subtracting the background near each peak.

Results and Discussion

Modification of matching circuit

After the Ar plasma was generated, the replacement of the Ar by N₂ was tried in a way similar to that reported in ICP-AES. However, the Ar plasma was soon extinguished even when only a small amount of N₂ was introduced into the outer gas. Therefore, the original load coil (30 mm i.d. and 2 turn) was replaced by the one with 25-mm i.d. and 3 turns to increase the RF coupling. Due to the modification of the load coil, the capacitance of the matching circuit had to be reduced for tuning. The ceramic capacitors that were originally connected in parallel to the vacuum (C₁, series) and the air (C₂, shunt) variable capacitors were removed. The variable ranges of the C₁ and C₂ changed from 95 -155 pF and 400 - 800 pF to 45 - 105 pF and 300 - 700 pF, respectively. After these modifications of the load coil and matching circuit, gas flows of the plasma became easily replaced by N₂ or O₂. With the addition of N₂ or O₂, the capacitance of C₁ was decreased and C₂ was increased to reduce the reflected power. These changes in the values of capacitors during the course of the gas replacement were similar to those reported in the generation of the N₂ plasma with the higher RF power.

The generation of the N₂ plasma was tried also by using an automatic tuning control for an ICP emission spectrometer (Seiko SPS 1100H, 2 kW max., 27.12 MHz, 25-mm i.d. and 3-turn load coil). The outer and carrier Ar gases could be completely replaced by N₂, but the time constant of the automatic tuning response had to be increased from the original setting. The shunt capacitor in this instrument was tuned manually during the conversion process.

Procedure for replacing the Ar to N₂ or O₂

The Ar plasma was first generated as usual and then the outer and carrier gases were slowly replaced by N₂. The Ar plasma was operated at the RF power of 1.3 kW and sampling depth of 7 mm. Before the introduction of N₂, the RF power was increased to 1.8 kW and the sampling depth was set to 0 mm. The plasma was repositioned before the gas conversion because an erratic discharge occurred between the plasma and the sampling orifice after the Ar gas was replaced by N₂. The orifice tip was located at ca. 1 mm inside of the torch at the sampling depth of 0 mm and this depth was most favorable for the highest sensitivity with the N₂ plasma. Since there are three gas flows, various combinations of the gas flows are possible depending on which flows are replaced by N₂ or O₂. Table 1 shows the gas flow rates for the combinations of the gases with which the plasmas could be operated in a stable way: values in parentheses are the flow rates of Ar that are not replaced by N₂ or O₂, and the others are the flow rates of N₂ or O₂. In this paper, the plasmas (a) to (h) in Table 1 are called N₂ or O₂ plasma for convenience, although it is not correct in a strict sense since they contain more or less Ar. The N₂ plasma (a) in Table 1, for example, is generated by slowly adding N₂ into the outer gas and minimizing the reflected power until the flow rate of N₂ reaches the value shown in Table 1 and then decreasing the Ar flow rate to zero. For the N₂ plasma (b) in Table 1, the carrier Ar gas is replaced by N₂ following the conversion of the outer gas. The conversion in reversed order was impossible. Only these two combinations, (a) and (b), were possible for the N₂ plasma, while 6 combinations, (c) to (h) in Table 1, were possible for the O₂ plasma. The conversion into O₂ was carried out in a way similar to the case of N₂, but the sampling depth was set to 2 mm. The gas conversion into O₂ was considerably easier than that into N₂. Moreover, it was possible to add O₂ into the intermediate gas up to 60% after the generation of the O₂ plasma (h) in Table 1. This is probably due to the fact that the dissociation energy of O₂ is lower than that of N₂. In the cases of (a), (c) and (f), the flow rate of intermediate Ar gas had to be increased to 21/min in order to prevent the top of an intermediate tube from melting.

With the introduction of N₂ or O₂ into the outer gas, the appearance of the plasmas became longer and thinner and the brightly shining core with a donut shape located near the plasma was moved toward the sampling orifice after the Ar gas was replaced by N₂. The orifice tip was located at ca. 1 mm inside of the torch at the sampling depth of 0 mm and this depth was most favorable for the highest sensitivity with the N₂ plasma.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Type</th>
<th>Gas flow rate / 1 min⁻¹</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Outer</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Ar</td>
<td>(14)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>N₂</td>
<td>a</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>19</td>
</tr>
<tr>
<td>O₂</td>
<td>c</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>g</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>15</td>
</tr>
</tbody>
</table>

Values in parentheses are flow rates of Ar not replaced by N₂ or O₂.

Table 1 Combination of gas flows for N₂ and O₂ plasmas
the load coil became shorter. The volume of the shining core became even smaller when both the outer and carrier gases were converted to N₂ or O₂ and the shape finally appeared like a ring.

No apparent effect of the oxidization or deterioration at the copper sampling and skimmer cones of the mass spectrometer was observed when the O₂ plasma was operated for several months.

Variation of ion signal intensities in gas-conversion process

The variations of various ion intensities including La⁺ as an analyte were measured during the conversion process from Ar to N₂, the results being shown in Fig. 1. The signal intensities were normalized by those with the Ar plasma. The conversion of the outer gas was followed by that of the carrier gas. The La⁺ intensity decreased drastically when N₂ was introduced into the outer gas, but the intensity was recovered to ca. 70% of that with Ar plasma after the carrier gas was replaced. LaO⁺, however, also increased when the carrier gas was replaced. Although the ArO⁺ decreased at first when the N₂ was introduced into the outer gas, the intensity again increased as the carrier gas was converted and finally became ca. 50% of that with the Ar plasma. Ar₂⁺, however, decreased at first and remained at low level. ArN⁺, on the other hand, increased significantly and finally became ca. 80 times. The increase in the intensity of Cu⁺, which originates from the copper sampling orifice, seems to be caused by the enhancement of the secondary discharge at the sampling orifice, although La₂⁺ increased only slightly.

Since it was possible to add O₂ into the intermediate gas after both the outer and carrier gases were replaced by O₂, the variations of the intensities of Y⁺, YO⁺ and ArO⁺ were measured as a function of the fraction of O₂ in the total flow rate of the intermediate gas (1.5 - 2.0 l/min). As shown in Fig. 2, the intensities of all these ions decreased with the increasing fraction of O₂. This may be partly due to the fact that the sampling depth was optimized before O₂ was introduced into the intermediate gas. No further experiments, however, were carried out, because little improvement of the sensitivity was expected by the addition of O₂ into the intermediate gas.

Mass spectra of N₂ and O₂ plasmas

Mass spectra measured with N₂ plasma (b), O₂ plasma (f) and Ar plasma operated under the condition in Table 1 are shown in Fig. 3. There is no significant difference in these spectra except that a large ArN⁺ peak is observed for the N₂ plasma. With the O₂ plasma, oxide ions of analytes inevitably become higher compared to other plasmas, but the ArO⁺ peak is relatively low.
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Intensities of several background ions were measured with the plasmas listed in Table 1. Their ratios to the corresponding intensities with the Ar plasma are shown in Table 3. The intensity of ArN+ is naturally strong with the N2 plasmas. The intensity of ArO+ is generally high with the O2 plasmas, but low for plasma (f). Ar2+ is considerably attenuated for all the types of the plasmas and significantly low for plasma (f). The intensity of Cu+ originated from the sampling orifice is higher than that with the Ar plasma for all the types of the N2 and O2 plasmas.

Signal to background (S/B) ratios of Co+, Y+ and In+ were improved only with O2 plasma (f) compared to the Ar plasma. With other plasmas (b, c and d), background intensities became relatively high, and consequently, S/B ratios were inferior to those with the Ar plasma.

Comparison of detection limits with Ar plasma

Detection limits of various elements with the ionization potential ranging from 3.94 (Cs) to 10.451 (I) eV were measured with the N2 (b) and O2 (f) plasmas in Table 1, because only these plasmas were considered to be practically useful. The detection limits were defined as the concentrations which yield signals of 2 times the standard deviations of the blank signals. For selenium, 80Se+ was measured for the N2 and O2 plasmas, while 78Se+ was measured for the Ar plasma and reduced to that of S°Se+ from natural abundance, because Ar2+ interfered with 80Se+.

The ratio of the detection limit with N2 or O2 plasma to that with the Ar plasma was calculated for each element. The ratios are plotted as a function of the ionization potential of elements, as shown in Fig. 4. The elements with the ratio less than one are more sensitive with the N2 or O2 plasma than with the Ar plasma. Apparently, the ratio increases with the increase in the ionization potential of elements. Lam and Horlick, however, reported that the degree of signal enhancement in the 5% N2−Ar mixed plasma does not depend on the ionization potential of elements. As shown in Fig. 4, the detection limits of several elements having the ionization potential less than 6–7 eV were superior to those with the Ar plasma. In ICP-AES, the Ar−N2 mixed and N2 plasmas operated at relatively low power have been reported to yield the

Comparison of ion signal intensities with Ar plasma

Signal intensities of Co+, Y+ and In+ were measured with the plasmas listed in Table 1 and their ratios to the corresponding intensities with the Ar plasma are shown in Table 3. Only the N2 plasma (b) and the O2 plasma (d) and (f) gave the analyte ion intensities comparable or superior to those with the Ar plasma. The O2 plasma (d), however, may not be considered as an O2 plasma because only the intermediate gas is replaced by O2.

Table 2 Signal intensities normalized by those with Ar plasma

<table>
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<th>Plasma</th>
<th>Type</th>
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<th>Y+</th>
<th>In+</th>
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<tbody>
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<td>a</td>
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<td>10⁻²</td>
<td>10⁻²</td>
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<tr>
<td></td>
<td>b</td>
<td>0.82</td>
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<tr>
<td>O2</td>
<td>c</td>
<td>0.18</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>1.4</td>
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<td>2.4</td>
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<tr>
<td></td>
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<td>10⁻³</td>
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</table>
detection limits inferior to those obtained with the pure Ar plasma by 1 to 2 orders of magnitude, especially for the spectral lines possessing high excitation energy. These results suggest that the low-power N2 and O2 plasmas are not such efficient ionization sources as the Ar plasma.

Comparing the detection limits for the N2 and O2 plasmas, the lower values were obtained with the O2 plasma for many elements. Barnes et al. measured the excitation temperature for the high-power N2 and O2 plasmas (3.2 - 4.5 kW, 27.12 MHz)\(^{1,2}\), reporting that a higher temperature was observed near the load coil with the O2 plasma than with the N2 plasma. The lower detection limits obtained with the O2 plasma than with the N2 plasma in this study might be explained by the difference of the temperatures of these plasmas.

In conclusion, the generation of the low-power O2 plasma is easier than that for N2. Among the low-power N2 and O2 plasmas examined, the O2 plasma in which the outer and carrier gases are replaced by O2 is the most sensitive and shows the least spectral interferences caused by Ar adducts, although oxide ion intensities increase. The cost for the gas consumption can be reduced to half by using N2 or O2 gases instead of Ar. The capability of the introduction of organic solvents into the plasma for mass spectrometry will be a more important feature of the O2 plasma, because the carbon deposit at the sampling orifice can be completely eliminated. The results for the introduction of organic solvents into ICP-MS with the O2 plasma will be reported in the near future.

References


(Received July 19, 1993)
(Accepted October 21, 1993)