Evaluation of the detection capability of a high power nitrogen microwave-induced plasma for both atomic emission and mass spectrometry[†]

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In order to evaluate the detection capability of a high power N_2-MIP (surface wave mode cavity) for AES and MS, a comparison of the detection limits between high power N_2-MIP-AES and Ar-ICP-AES was conducted under almost the same plasma operating conditions and with the same measurement systems. Moreover, a comparison of the detection limits between high power N_2-MIP-MS and Ar-ICP-MS was also carried out under optimum operating conditions for each instrument. The detection limits (3σ) were established as the detection capability for both plasma systems using a total of 55 wavelengths (atom and ion lines) for 21 elements for AES and a total of 38 *m/z* values for 22 elements for MS. The detection limits obtained for N_2-MIP-AES (0.4–3000 ng ml^{-1}) were from one to two orders of magnitude worse than those for Ar-ICP-AES. On the other hand, the detection limits for N_2-MIP-MS (1–3600 pg ml^{-1}) were almost the same or one order of magnitude worse than those for Ar-ICP-MS. The detection capability of a high power N_2-MIP was evaluated both from results in this work and from those given previously.

Keywords: High power nitrogen microwave-induced plasma atomic emission spectrometry; high power nitrogen microwave-induced plasma mass spectrometry; argon inductively coupled plasma atomic emission spectrometry; argon inductively coupled plasma mass spectrometry; detection limit; excitation energy; ionization energy; background

Recently, AES and MS combined with an Ar-ICP source have been applied to various fields as methods of trace element analysis.[1–12] However, the Ar-ICP has several limitations, for example, polyatomic ions related to the plasma sustained in Ar gas interfere with the analytes in MS. In order to remove these limitations, plasma sources sustained by gases other than Ar or mixed gases with Ar have been developed and investigated by several workers. For example, He-ICP,[13–17] N_2-ICP,[18] O_2-ICP,[19] Air-ICP,[20] Ar–N_2-ICP,[21–31] Ar–O_2-ICP,[23,25,32–37] Ar–air-ICP,[33] Ar–H_2-ICP,[27] and several types of MIPs[37–42] have been examined for this purpose.

A high power MIP source using an Okamoto cavity (2.45 GHz, maximum 1.5 kW) can be sustained by He, N_2 and air at atmospheric pressure. The plasma is doughnut shaped just the same as the Ar-ICP and it enables the introduction of sample aerosols to be made directly into the center of the plasma.[43,44] When N_2 is used for the plasma sustaining gas, interferences due to Ar associated species such as $^{40}Ar^{16}O^+$, $^{40}Ar^{35}Cl^+$ and $^{40}Ar_2^+$ do not occur in MS, thus the primary isotopes $^{56}Fe^+$, $^{75}As+$ and $^{80}Se^+$ can be used in determinations.[45,46] Furthermore, the running costs become lower than those of an Ar-ICP. From these advantages mentioned above, it is expected that a high power MIP source would be applicable to various areas of trace element analysis, instead of the Ar-ICP source. However, there have been few reports of both AES and MS using this source.[47–50] The purpose of the present work is to evaluate the detection capability of a high power N_2-MIP for both AES and MS.

EXPERIMENTAL

Instrumentation

The instrumentation used for the AES work has been described in a previous paper[51] and the instruments for N_2-MIP-MS and Ar-ICP-MS were a P-6000 (Hitachi, Ibaraki, Japan) and an HP-4500 (Yokogawa Analytical Systems, Tokyo, Japan), respectively. The plasma operating conditions and the measurement systems for N_2-MIP-AES and Ar-ICP-AES are summarized in Table 1. In the present work, both plasma sources were operated under almost the same conditions. The detection limits were measured under the same measurement systems with a PMT (Model R919, Hamamatsu Photonics, Hamamatsu, Japan). The plasma operating conditions and measurement systems for N_2-MIP-MS and Ar-ICP-MS are summarized in Table 2. For MS the detection limits were measured under optimum operating conditions for each plasma and using much the same measurement conditions (integration time).

Reagents

Standard solutions (1000 μg ml^{-1}) for each element were purchased from Kanto Chemical Co. (Tokyo, Japan). Sample solutions were prepared by serially diluting the standard solutions with 0.1 mol l^{-1} HNO$_3$ solution. The HNO$_3$ used was 68% of high purity grade (Kanto Chemical Co.), and the water used was Milli-Q purified water that was prepared by further purification of de-ionized water by a Milli-Q system (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan).

Procedures to determine detection limits

In order to determine the detection limits (3σ) for AES, the spectral line intensity of the standard solutions and the background intensity of the blank solution (0.1 mol l^{-1} HNO$_3$) were recorded on a chart recorder through the low pass filter (less than 5 Hz) with 96 decibel/octave. The peak-to-peak variation of the background intensity recorded on a chart recorder was considered to be 5σ. For MS, the measurement of standard solutions was repeated three times and the measurement of the blank solution (0.1 mol l^{-1} HNO$_3$) was repeated ten times. The 1σ value was obtained from the variation of the blank signals. The detection limits were calculated as the concentration which produced a signal equal to 3σ for both AES and MS.

Selection of analytical wavelengths and analytical masses

The analytical wavelengths were chosen so as to obtain the highest signal to background ratio for Ar-ICP-AES.[52] Additional wavelengths were also chosen which have low excitation energies and are not overlapped by nitrogen related

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Table 1 Operating conditions and measurement parameters for N₂-MIP-AES and Ar-ICP-AES

Parameter	N₂-MIP	Ar-ICP
Plasma source—		
Frequency	2.45 GHz	27.12 MHz
Incident power	1.3 kW	1.3 kW
Outer gas	11.0 l min^{-1}	16.0 l min^{-1}
Intermediate gas	—	1.0 l min^{-1}
Aerosol carrier gas	1.0 l min^{-1}	1.0 l min^{-1}
Uptake rate	1.6 ml min^{-1}	1.6 ml min^{-1}
Monochromator—		
Focal length	1 m	
Grating	2400 grooves mm^{-1}	
Slit height	2 mm	
Slit width	50 μm	
Detector—		
Photomultiplier tube	R919	

background spectra, for N₂-MIP-AES. The m/z values were chosen so that no interferences were caused by the plasma sustaining gases and also to represent high isotopic abundances for both N₂-MIP-MS and Ar-ICP-MS, respectively.

RESULTS AND DISCUSSIONS

Comparison of the detection limits between high power N₂-MIP-AES and Ar-ICP-AES

The obtained detection limits (3σ) for the full 55 wavelengths for 21 elements are shown in Table 3(a)–(d) for both high power N₂-MIP-AES and Ar-ICP-AES. The 21 elements are classified into four groups depending on the ionization energy. Table 3(a) shows the detection limits (DL) for the elements with an ionization energy of less than 7.0 eV for both plasmas. The detection limits range from 1 to 300 ng ml^{-1} for the N₂-MIP and from 0.1 to 70 ng ml^{-1} for the Ar-ICP.

As shown in a previous paper,[51] the elements with an ionization energy below 7.0 eV are ionized almost 100% in both plasmas. In other words, excited analyte ions of these elements prevail in both plasmas. Therefore, it is concluded that the detection limits of ion lines are better than those of atom lines in both plasmas. It can be expected that the spectral line intensity of an ion becomes larger with an increase in plasma temperature. Hence, it can be expected that the detection limits of the Ar-ICP would be better than those of the N₂-MIP, because the temperature of the Ar-ICP (7500 K) is higher than that of the N₂-MIP (5400 K).[51] From the ratios

Table 2 Operating conditions and measurement parameters for N₂-MIP-MS and Ar-ICP-MS

Parameter	N₂-MIP	Ar-ICP
Plasma source—		
Frequency	2.45 GHz	27.12 MHz
Incident power	1.3 kW	1.3 kW
Outer gas	15.0 l min^{-1}	15.0 l min^{-1}
Auxiliary gas	—	1.0 l min^{-1}
Aerosol carrier gas	1.3 l min^{-1}	1.2 l min^{-1}
Uptake rate	0.3 l min^{-1}	0.35 ml min^{-1}
Mass spectrometer—		
Mass filter	Quadrupole	Quadrupole
Measurment mode	Peak hopping	Peak hopping
Integration time per m/z	3.3 s	3.3 s
Repetition of sample	3 times	3 times
Repetition of blank	10 times	10 times
Detector—	Channeltron	Electron multiplier
	4870V	AF 573 (M 67)
	Galileo Electr-Optics	ETP

of the detection limits, the detection limits of N₂-MIP-AES are 1–12 and 5–8 fold worse than those obtained by Ar-ICP-AES for atom (MIP/ICP of atom line) and ion lines (MIP/ICP of ion line), respectively. Scrutiny reveals that the detection limit of N₂-MIP-AES for Cr II with an excitation energy of 6.03 eV is exceptionally worse (about 60-fold higher) than that of Ar-ICP-AES. From this result, it is considered that the N₂-MIP has lower tolerance to excite elements with a high excitation energy compared with the Ar-ICP. This fact is also attributed to the difference in temperatures between the N₂-MIP and the Ar-ICP. From the ratios of the optimum detection limits, it can be concluded that the detection capability of N₂-MIP-AES is 1–10 fold lower than that of Ar-ICP-AES.

The detection limits for the elements with an ionization energy between 7.0 and 7.5 eV are shown in Table 3(b). The detection limits range from 10 to 3000 ng ml^{-1} for the N₂-MIP and from 0.5 to 350 ng ml^{-1} for the Ar-ICP. As shown in a previous paper,[51] the degree of ionization for these elements is 80–90% in the N₂-MIP and almost 100% in the Ar-ICP. Therefore, the detection limits of ion lines are better than those of atom lines for both plasmas. It can be seen that the detection limits for Ar-ICP-AES are better than those for N₂-MIP-AES, just as shown by the results in Table 3(a). It is also considered that the reason is attributed to the difference in temperature in the two plasmas. The ratios of the detection limits for N₂-MIP-AES are 0.5–10- and about 20-fold worse than those for Ar-ICP-AES for atom and ion lines, respectively. Because the ion lines of Pb, Sn and Mo have relatively high excitation energies (7.37, 7.05 and 6.13 eV, respectively), the detection limits of ion lines for N₂-MIP-AES are extremely bad compared with those for Ar-ICP-AES. On the contrary, in the case of Ar-ICP-AES, the detection limits for Pb II, Sn II and Mo II are better than those of the atom lines. From these results, it is also considered that the N₂-MIP has lower tolerance to excite elements with a high excitation energy compared with the Ar-ICP. In addition, from the ratios of the optimum detection limits, it can be concluded that the detection capability of N₂-MIP-AES is 1–18-fold lower than that of Ar-ICP-AES.

The detection limits for the elements with an ionization energy between 7.5 and 8.0 eV are shown in Table 3(c). The detection limits range from 2 to 2000 ng ml^{-1} for N₂-MIP-AES and 0.1 to 1000 ng ml^{-1} for Ar-ICP-AES. As shown in a previous paper,[51] the degrees of ionization for these elements are in the range from 50 to 80% in the N₂-MIP and from 90 to 95% in the Ar-ICP. In general, the ion lines for the elements with high ionization energy tend to have a high excitation energy. In N₂-MIP-AES, therefore, the detection limits for Co II, Cu II, Ni II and Ag II with high excitation energies are worse than those of atom lines. From these results, it is seen that the N₂-MIP does not have enough energy to excite an element with an excitation energy of more than 5.5 eV. However, the detection limits for Fe II and Mg II with relatively low excitation energy are better than those of the atom lines. On the other hand, the detection limits of the Ar-ICP for both atom and ion lines are better than those of N₂-MIP-AES. From the ratios of the optimum detection limits, it can be concluded that the detection capability of N₂-MIP-AES is 1–10-fold lower than that of Ar-ICP-AES.

In Table 3(d) are shown the detection limits for elements with an ionization energy of more than 8.0 eV. The observed detection limits are 30–2000 ng ml^{-1} for N₂-MIP-AES and 2–110 ng ml^{-1} for Ar-ICP-AES. As shown in a previous paper,[51] the degrees of ionization of these elements are in the range from 0.3 to 25% in the N₂-MIP and from 15 to 85% in the Ar-ICP. Because the excitation energy becomes higher with an increase in the ionization energy of the elements, the detection limits of atom lines are better than those of ion lines in both plasmas. The excited analyte atoms prevail compared

Table 3 Detection limits (3σ)

Ionization energy/ eV	Element and line	Wave-length/ nm	Excitation energy/ eV	D L of MIP/ ng ml^{-1}	D L of ICP/ ng ml^{-1}	Element and line	Wave-length/ nm	Excitation energy/ eV	D L of MIP/ ng ml^{-1}	D L of ICP/ ng ml^{-1}	MIP/ICP of atom line	MIP/ICP of ion line	MIP/ICP under optimum
		Atom line						Ion line					
(a) Elements with ionization energy less than 7.0 eV—													
5.139	Na I	589.0	2.11	46	5.8	—	—	—	—	—	7.9	—	7.9
5.986	Al I	309.3	4.02	98	21	—	—	—	—	—	4.7	—	1.2
5.986	Al I	396.2	3.14	12	10	—	—	—	—	—	1.2	—	1.2
6.113	Ca I	422.7	2.93	3.7	1.1	Ca II	393.4	3.15	0.38	0.06	3.4	6.3	6.3
6.740	V I	437.9	3.13	27	20	V II	292.4	4.63	11	2.0	1.4	5.6	6.8
—	—	—	—	—	—	V II	309.3	4.40	8.8	1.3	—	6.8	6.8
6.766	Cr I	357.9	3.46	90	7.7	Cr II	205.6	6.03	280	4.6	12	61	7.3
6.766	Cr I	429.0	2.89	24	18	Cr II	267.7	6.18	25	3.3	1.3	7.6	7.3
6.820	Ti I	398.2	3.11	120	66	Ti II	334.9	3.74	4.3	0.9	1.8	4.8	4.8
(b) Elements with ionization energy between 7.0 and 7.5 eV—													
7.099	Mo I	390.3	3.17	180	18	Mo II	202.0	6.13	340	6.0	10	57	30
7.344	Sn I	235.5	5.47	1600	340	Sn II	190.0	7.05	2900	44	4.7	66	2.0
7.344	Sn I	284.0	4.78	87	180	—	—	—	—	—	0.48	—	2.0
7.416	Pb I	217.0	5.71	1000	110	Pb II	220.4	7.37	2600	44	9.1	59	1.8
7.416	Pb I	405.8	4.38	80	84	—	—	—	—	—	0.95	—	1.8
7.416	Pb I	283.3	4.37	130	130	—	—	—	—	—	1.0	—	1.8
7.435	Mn I	279.5	4.44	12	8.6	Mn II	257.6	4.81	6.9	0.4	1.4	17	17
7.435	Mn I	403.1	3.08	18	9.7	—	—	—	—	—	1.9	—	17
(c) Elements with ionization energy between 7.0 and 7.5 eV—													
7.576	Ag I	328.1	3.78	6.5	2.3	Ag II	243.8	9.93	—	140	2.8	—	2.8
7.576	Ag I	338.3	3.66	14	6.9	Ag II	233.1	10.36	—	890	2.0	85	2.8
7.635	Ni I	232.0	5.34	54	14	Ni II	221.6	6.63	580	6.8	3.9	25	3.8
7.635	Ni I	361.9	3.85	23	38	Ni II	231.6	6.38	150	6.0	0.60	8.6	3.8
7.646	Mg I	285.2	4.34	2.2	1.3	Mg II	279.6	4.43	0.60	0.07	1.7	—	8.6
7.726	Cu I	324.8	3.82	2.3	2.0	Cu II	204.4	8.78	—	33	1.2	—	1.2
—						Cu II	224.7	8.23	1800	6.9	—	260	1.2
7.860	Co I	345.4	4.02	15	29	Co II	239.0	5.60	40	4.2	0.52	9.5	3.8
—						Co II	228.6	5.84	60	4.0	—	15	3.8
7.870	Fe I	372.0	3.33	79	54	Fe II	259.9	4.77	13	1.6	1.5	8.1	8.1
—						Fe II	238.2	5.20	40	3.2	—	12	8.1
(d) Elements with ionization energy more than 8.0 eV—													
8.993	Cd I	228.8	5.41	24	1.8	Cd II	226.5	5.47	110	2.9	13	38	13
8.993		—	—	—	—	Cd II	214.4	5.78	190	5.0	—	38	13
9.394	Zn I	213.9	5.80	50	2.1	Zn II	206.2	6.01	120	2.5	24	48	24
9.394		—	—	—	—	Zn II	202.5	6.12	110	3.2	—	34	24
9.752	Se I	196.1	6.32	780	110	—	—	—	—	—	7.1	—	7.1
9.810	As I	193.8	6.40	840	75	—	—	—	—	—	11	—	11
9.810	As I	197.2	6.29	1200	100	—	—	—	—	—	12	—	12
10.486	P I	215.0	7.18	1900	94	—	—	—	—	—	20	—	20

with excited analyte ions, therefore, the spectral line intensity of atoms becomes higher than that of ions. From the ratios of the optimum detection limits, it can be concluded that the detection capability of N_2-MIP-AES is 7–25-fold lower than that of Ar-ICP-AES.

It can be seen that the difference in detection capability between N_2-MIP-AES and Ar-ICP-AES, which is shown in Table 3(d), is larger than that shown in Table 3(a)–(c). The ratio of the detection limits of N_2-MIP to Ar-ICP as a function of an ionization plus excitation energy for both atom and ion lines is shown in Fig. 1. The differences in capabilities to excite various elements can be evaluated for both plasmas. From Fig. 1, it is clear that the detection limits of ion lines for N_2-MIP-AES are 10–100-fold worse than those for Ar-ICP-AES with an ionization plus excitation energy of greater than 12.5 eV. In other words, the N_2-MIP does not have enough energy to excite ion lines with an ionization plus excitation energy of more than 12.5 eV. For atom lines, however, the difference is small and the detection limits are 1–25-fold worse than those of the Ar-ICP. Because the temperature of the N_2-MIP is lower than that of the Ar-ICP,[51] the number density of excited analyte atoms is prevalent in the N_2-MIP compared with in the Ar-ICP. This effect reduces the difference in emission intensity of atom lines between the N_2-MIP and the Ar-ICP.

Shown in Fig. 2 are the ratios of the optimum detection limits for the N_2-MIP and the Ar-ICP as a function of ionization energy of the elements. It is clear from Fig. 2 that the detection limits for N_2-MIP-AES are 1–10- and 7–25-fold worse than those for Ar-ICP-AES for elements with an ionization energy of less than 8.0 and more than 8.0 eV, respectively, as mentioned above. Therefore, it can be assumed that the N_2-
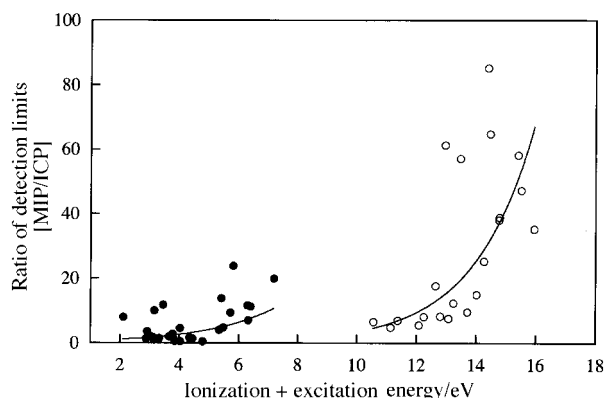

Fig. 1 Ratio of the detection limits of N_2-MIP-AES to Ar-ICP-AES as a function of the ionization plus excitation energy (eV) using atom and ion lines. ●, ratio of atom lines; and ○, ratio of ion lines.
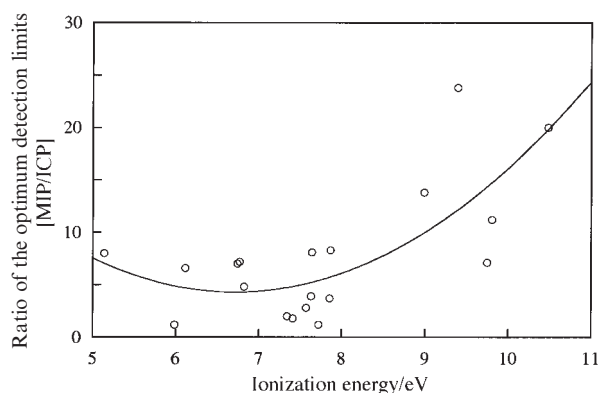

Fig. 2 Ratio of the optimum detection limits of N_2-MIP-AES to Ar-ICP-AES as a function of the ionization energy (eV) of elements.

MIP has difficulty in exciting elements with an ionization energy of more than 8.0 eV compared with the Ar-ICP. These experimental results can be explained by the shift in ionization equilibrium and the difference in temperature between the N_2-MIP and the Ar-ICP.

Effects of background spectra for AES

It is considered that the main reason for the difference in detection limits between N_2-MIP-AES and Ar-ICP-AES is attributed to the difference in the plasma temperature. However, the detection limit is not only determined by the emission intensity but also by the background emission intensity. For example, for Pb I (405.8 nm) in Table 3(b) and Co I (345.4 nm) in Table 3(c), the detection limits for N_2-MIP-AES are better than those for Ar-ICP-AES. The experimental results can be explained by the background effects. The background around the analytical lines of Pb I (405.8 nm) and Co I (345.4 nm) of the N_2-MIP are simple compared with that of the Ar-ICP, which was shown in a previous paper.[51] The difference in the background is attributed to the plasma sustaining gases of the N_2-MIP and the Ar-ICP. The Ar-ICP has a background of continuum emission, whereas in N_2-MIP-AES, there is no background of continuum emission although there are large N_2 related molecular bands. As the background emission intensity influences the detection limits, the best analytical line of the analyte should be chosen for AES.

Comparison of detection limits between high power N_2-MIP-MS and Ar-ICP-MS

The detection limits obtained (3σ) for the full 38 m/z values for 22 elements are shown in Table 4(a)–(c) for both high power N_2-MIP-MS (P-6000) and Ar-ICP-MS (HP-4500). The 22 elements are classified into three groups depending on the ionization energy of each element. The detection limits for the elements with an ionization energy of less than 7.0 eV are shown in Table 4(a). The detection limits are 1–1000 and 0.5–100 pg ml^{-1} for N_2-MIP-MS and Ar-ICP-MS, respectively, except for $^{43}Ca^+$. As shown in a previous paper,[51] elements with an ionization energy of less than 7.0 eV are ionized almost 100% in both plasmas. Therefore, the detection limits for both plasma MS instruments should be almost the same. However, it is shown from the ratio of detection limits (MIP/ICP), that the detection limits for $^{23}Na^+$, $^{27}Al^+$ and $^{53}Cr^+$ for N_2-MIP-MS were about 6–10-fold worse than those for Ar-ICP-MS. It is considered that the differences in the detection limits for $^{23}Na^+$ and $^{27}Al^+$ were caused by the polyatomic ions of $^{11}B^{12}C^+$ and $^{11}B^{16}O^+$, respectively. The $^{11}B^+$ is probably due to the spray chamber, and $^{12}C^+$ and $^{16}O^+$ are from the Ar gas, air entrainment and sample solutions. Moreover, if the sampling cone is polluted by boron, there is a possibility boron associated polyatomic ions will exist in the background signal. Furthermore, it was also considered that the blank solution of 0.1 mol l^{-1} HNO$_3$ may be contaminated by boron from the glass flask.

For Cr, the detection limit of $^{52}Cr^+$ was better than $^{53}Cr^+$ in N_2-MIP-MS. On the contrary, the detection limit of $^{52}Cr^+$ was worse than $^{53}Cr^+$ in Ar-ICP-MS. As the isotopic abundance of $^{52}Cr^+$ (83.79%) is higher than $^{53}Cr^+$ (9.501%), the detection limit of $^{52}Cr^+$ should be better than that of $^{53}Cr^+$. Because the polyatomic ion of $^{40}Ar^{12}C^+$ interfered with $^{52}Cr^+$, the detection limit for $^{52}Cr^+$ was worse than that of $^{53}Cr^+$ in the case of Ar-ICP-MS.

It is shown that a detection limit for $^{40}Ca^+$ was not obtained by Ar-ICP-MS, because $^{40}Ca^+$ was suffered from interference from $^{40}Ar^+$. Therefore the determination of $^{43}Ca^+$ was performed in Ar-ICP-MS instead of $^{40}Ca^+$. However, the detection limit obtained was very bad (1400 pg ml^{-1}) because the

Table 4 Detection limits (3σ)

Element	m/z	Ionization energy/ eV	Detection limit/ pg ml^{-1} N$_2$-MIP-MS (P-6000)	Ar-ICP-MS (HP-4500)	MIP/ICP	MIP/ICP under optimum
(a) Elements with ionization energy less than 7.0 eV—						
Na	23	5.139	4.7	0.79	5.9	5.9
Al	27	5.986	850	120	7.1	7.1
Ca	40	6.113	46	—	—	0.03
	43	—	3600	1400	2.6	—
V	51	6.740	1.2	0.49	2.4	2.4
Cr	52	6.766	11	14	0.8	2.5
	53	—	45	4.5	10	—
Ti	48	6.820	5.5	3.4	1.6	1.6
(b) Elements with ionization energy between 7.0 and 8.0 eV—						
Mo	98	7.099	4.6	0.83	5.5	5.5
Sn	118	7.344	4.4	0.62	7.1	7.6
	119	—	4.6	0.58	7.9	—
	120	—	3.4	2.2	1.5	—
Pb	206	7.416	5.1	1.3	3.9	2.6
	208	—	2.6	1.9	1.4	—
Mn	55	7.435	2.6	1.3	2.0	2.0
Ag	107	7.576	6.0	1.7	3.5	2.4
	109	—	3.8	1.6	2.4	—
Ni	60	7.635	6.8	2.0	3.4	3.4
Mg	24	7.646	3.7	2.6	1.4	1.4
Cu	63	7.726	12	9.0	1.3	1.3
	65	—	22	11	2.0	—
Co	59	7.860	1.4	0.19	7.4	7.4
Fe	54	7.870	24	170	0.14	0.03
	56	—	5.4	900	0.006	—
	57	—	45	240	0.19	—
(c) Elements with ionization energy more than 8.0 eV—						
Sb	121	8.639	4.2	2.6	1.6	1.6
	123	—	5.3	4.3	1.2	—
Cd	111	8.993	5.6	3.5	1.6	3.3
	112	—	7.0	1.7	4.1	—
	114	—	7.0	2.0	3.5	—
Zn	64	9.394	28	5.5	5.1	5.0
	66	—	36	6.9	5.2	—
Se	77	9.752	400	33	12	2.4
	78	—	170	170	1.0	—
	80	—	78	—	—	—
	82	—	120	41	3.0	—
As	75	9.810	79	4.1	19	19
P	31	10.486	—	200	—	—

isotopic abundance of $^{43}Ca^+$ is very low (0.135%). On the contrary, using N$_2$-MIP-MS $^{40}Ca^+$ could be observed and the detection limit obtained was better (46 pg ml^{-1}) than that for $^{43}Ca^+$ by Ar-ICP-MS. However, because the isotopic abundance of $^{43}Ca^+$ is very low as mentioned above, the detection limit for $^{43}Ca^+$ in N$_2$-MIP-MS was worse (3600 pg ml^{-1}) compared with that of Ar-ICP-MS. From this result, it is suggested that N$_2$-MIP-MS is very useful for the determination of trace amounts of Ca compared with Ar-ICP-MS.

From the ratios of the optimum detection limits (MIP/ICP under optimum) it can be seen that the detection limits of the elements with an ionization energy of less than 7.0 eV were almost the same or only 2–3-fold higher in N$_2$-MIP-MS compared with those of Ar-ICP-MS, except for $^{23}Na^+$ and $^{27}Al^+$.

In Table 4(*b*) are shown the detection limits of elements with an ionization energy of between 7.0 and 8.0 eV. The detection limits ranged from 3 to 50 and 0.2 to 900 pg ml^{-1} in N$_2$-MIP-MS and Ar-ICP-MS, respectively. As shown in a previous paper,[51] these elements are 50–90% ionized in the N$_2$-MIP and more than 90% in the Ar-ICP. It is expected from the differences in the degrees of ionization that the detection limits for N$_2$-MIP-MS should be almost the same or 2–3-fold worse

than those for Ar-ICP-MS. From Table 4(*b*), it can be seen that the obtained detection limits for Fe in Ar-ICP-MS were very bad compared with those of N$_2$-MIP-MS. It is considered that the reason for this was caused by Ar associated polyatomic ions of $^{40}Ar^{14}N^+$, $^{40}Ar^{16}O^+$ and $^{40}Ar^{16}OH^+$. Whereas, the detection limits obtained for $^{54}Fe^+$, $^{56}Fe^+$ and $^{57}Fe^+$ in N$_2$-MIP-MS were good, because the polyatomic ion interferences at the m/z 54, 56 and 57 were not observed in N$_2$-MIP-MS. It is also seen from the ratios of the optimum detection limits of Table 4(*b*) that the detection limits for N$_2$-MIP-MS were 1–8-fold worse compared with those for Ar-ICP-MS, except for Fe. In particular, it can be stressed that high power N$_2$-MIP-MS shows an excellent advantage for the determination of trace levels of Fe compared with Ar-ICP-MS.

The detection limits of elements with an ionization energy of more than 8.0 eV are shown in Table 4(*c*). The detection limits ranged from 4 to 400 and 2 to 200 pg ml^{-1} for N$_2$-MIP-MS and Ar-ICP-MS, respectively. As shown in a previous paper,[51] the degrees of ionization of these elements are in the range 0.3–25% in the N$_2$-MIP and 15–85% in the Ar-ICP. Therefore, it is expected that the detection limits obtained for N$_2$-MIP-MS become about one order of magnitude worse than those for Ar-ICP-MS. The differences in the detection

limits obtained were in the range 1–20-fold between N_2-MIP-MS and Ar-ICP-MS. However, if $^{77}Se^+$ and $^{75}As^+$ are excluded, it is shown that the detection limits for N_2-MIP-MS are almost the same or 2–5-fold worse compared with those for Ar-ICP-MS for elements with an ionization energy of less than about 9.5 eV.

One of the merits of N_2-MIP-MS is that Se can be measured using the primary isotope without any interferences. Because the polyatomic ion of $^{40}Ar_2^+$ interferes at m/z 80, the determination of Se with the primary isotope is impossible by Ar-ICP-MS. As shown from ratios of the optimum detection limits the detection limit for Se in N_2-MIP-MS was about 2-fold worse than that of Ar-ICP-MS.

From the ratios of the optimum detection limits (MIP/ICP under optimum), the differences in the detection limits obtained were in a range of from 1 to 20-fold between N_2-MIP-MS and Ar-ICP-MS, which is just the same as the ratios of the detection limits (MIP/ICP). It is noted that $^{31}P^+$ was not determined by N_2-MIP-MS, because the polyatomic ion of $^{14}N^{16}OH^+$ caused by the N_2 plasma sustaining gas, air entrainment and sample solution seriously interfere at m/z 31.

The ratios of calculated degrees of ionization of the Ar-ICP to the N_2-MIP for each element as a function of ionization energy are shown in Fig. 3. The values were calculated using the plasma temperature and the electron number density described in a previous paper.[51] The experimentally obtained detection limit ratios of N_2-MIP-MS to Ar-ICP-MS at the same mass (MIP/ICP) is shown in Fig. 4. These plotted data are the elements without any serious intereferences due to polyatomic ions caused by the plasma sustaining gases for each plasma source. It is seen that the theoretical ionization ratio values show the same trend as experimentally obtained detection limit ratio values.
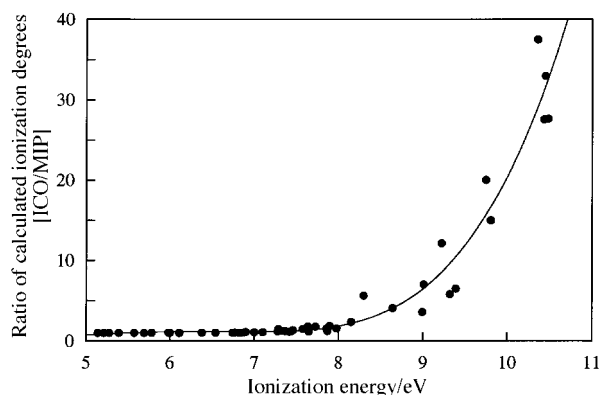
From these results, it was confirmed that the differences in the detection capabilities between N_2-MIP-MS and Ar-ICP-MS could be discussed in terms of the differences in the plasma temperature and the electron number density of the N_2-MIP and the Ar-ICP, which has been described in a previous paper.[51]

CONCLUSIONS

It is concluded from the optimum ratios of the detection limits that the detection capabilities of N_2-MIP-AES are 1–10- and 7–25-fold lower than those of Ar-ICP-AES for the elements with ionization energies of less than 8.0 and more than 8.0 eV, respectively. On the other hand, the detection capabilities of N_2-MIP-MS are almost the same or 2–8-fold lower compared with those of Ar-ICP-MS for analytes with an ionization energies of less than 9.5 eV if serious spectral interferences do not exist. However, for the elements with ionization energies of more than 9.5 eV, the detection capability of N_2-MIP-MS is one order of magnitude lower than that of Ar-ICP-MS. The N_2-MIP-MS has an advantage for the determination of $^{40}Ca^+$, $^{52}Cr^+$, $^{56}Fe^+$ and $^{80}Se^+$, using primary isotope abundances without any spectral interferences due to Ar associated polyatomic ions. Because the background spectra influence the detection capability of AES and MS, a judicious choice of the analytical lines and m/z values is necessary for AES and MS, respectively.

Fig. 3 Ratio of calculated degrees of ionization of the Ar-ICP to the N_2-MIP as a function of the ioniztion energy (eV) of elements.
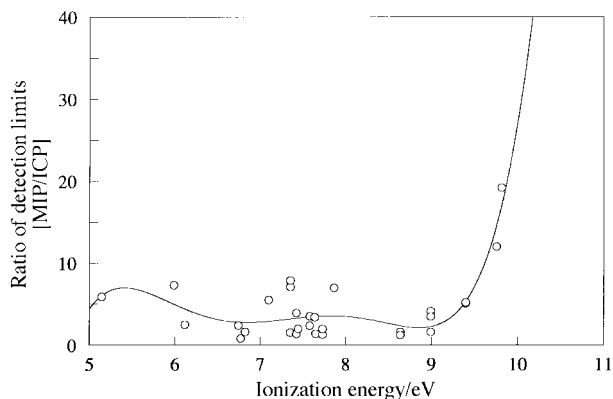

Fig. 4 Ratio of the detection limits of N_2-MIP-AES to Ar-ICP-AES as a function of the ionization energy (eV) of elements.

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