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1 Comparison of signal enhancement by co-existing carbon and by co-existing bromine in

2 inductively coupled plasma mass spectrometry

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5 Takashi Nakazawa, Daisuke Suzuki, Hironori Sakuma and Naoki Furuta*

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7 *Faculty of Science and Engineering, Department of Applied Chemistry, Chuo University,*

8 *1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan*

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29 *To whom correspondence should be sent.

30 E-mail address: nfuruta@chem.chuo-u.ac.jp

31 Tel & Fax: +81-3-3817-1906

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1   In inductively coupled plasma (ICP) mass spectrometry, signal enhancement by
2   co-existing carbon results from multiple factors. To elucidate the signal enhancement
3   factors, we compared the effects of co-existing carbon and co-existing bromine, which
4   have similar ionization energies (C, 11.26 eV; Br, 11.81 eV). We eliminated the effect of
5   sample introduction efficiency, changes in which are considered to be one reason for
6   signal enhancement, by using two nebulizers. The intensities of the P, I, S, As, Se and B
7   signals were enhanced when a multi-element solution was introduced into the ICP from
8   one nebulizer and a carbon solution was introduced from the other. No signal
9   enhancement was observed by co-existing bromine. We focused on the bond energies of
10 the oxides as a possible explanation for the difference between the results for carbon
11 and bromine. The carbon oxide has a higher bond energy than the bromine oxide, and
12 therefore carbon reduces analyte oxides more readily than bromine does. We also
13 considered the effects of the bond energies of the analyte oxides, as well as the effects
14 of the degree of analyte ionization in the ICP, on signal enhancement. Signal
15 enhancement was observed for analytes that were less than 60% ionized in the ICP and
16 whose oxide bond energies exceeded 450 kJ mol^{-1}. Iodine was an exception; signal
17 enhancement was observed for I (ionization degree, 29.85%), even though the bond
18 energy of iodine oxide is only 240 kJ mol^{-1}. Therefore, charge transfer could not be
19 eliminated as a cause of signal enhancement.

20

21   **1 Introduction**

22

23   In inductively coupled plasma mass spectrometry (ICP-MS), signal enhancement by
24   co-existing carbon has been reported by several research groups.[1–9] In particular,
25   enhancements of the signals for P, S, As and Se, which have first-ionization energies of
26   9–11 eV, have been observed.[10–12] The enhancement is generally accepted as being due
27   to charge transfer (CT) between the analyte atom (M) and positively charged carbon
28   ions or carbon-H ions (C^{+}-species) in the matrix:[13,14]

29

30   $$C^{+}\text{-species} \; + \; M \; \rightarrow \; C\text{-species} \; + \; M^{+} \qquad (1)$$

31
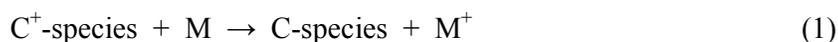
32   CT is possible only when the ionization energy of the analyte is similar to that of C
33   (11.26 eV) or CH (10.64 eV). However, signal enhancement cannot be explained by eqn
34   (1) alone. One reason is that signal enhancement has been observed not only in ICP-MS
35   but also in ICP optical emission spectrometry (OES).[15–18] In ICP-MS analyte ions are
36   observed and in ICP-OES the emission of analyte atoms is observed. If CT affects

1 ionization degree of analytes and decrease analyte atoms, the signal of ICP-OES should

2 be suppressed. Moreover, the effects of co-existing carbon on sample nebulization

3 efficiency, optimal carrier gas flow rate and plasma temperature have also been

4 suggested as causes of signal enhancement or suppression.[1,19-22]

5   In this study, to investigate the cause of signal enhancement due to co-existing

6 carbon, we compared the signal enhancement effects on analyte signals by co-existing

7 bromine (ionization energy, 11.81 eV) and by co-existing carbon (ionization energy,

8 11.26 eV). Specifically, a carbon- or bromine-containing sample solution and a

9 multi-element solution were introduced into an ICP-MS separately via concentric and

10 ultrasonic nebulizers, respectively, and the resulting aerosols were merged upstream of

11 the plasma torch. This sample introduction system eliminates changes in aerosol size

12 produced by nebulizer as a reason for signal enhancement effects. To elucidate the

13 enhancement mechanism, we also considered the relative bond energies of analyte

14 oxides, carbon oxide and bromine oxide, as well as the degree of ionization of the

15 analytes in the ICP.

16

17 **2 Experimental**

18

19 **2.1 Reagents and samples**

20

21 Ultrapure water with a resistivity > 18.2 MΩ cm was obtained from a Milli-Q system

22 (Millipore, Tokyo, Japan) and used throughout this work for preparation of all solutions.

23 A stock solution containing carbon at a concentration of 10 mg mL^{-1} was prepared by

24 dissolving urea ($CO(NH_2)_2$, Kanto Chemical Co., Inc., Tokyo, Japan) in ultrapure water.

25 For pH effects on signal enhancement, oxalic acids dehydrate (($COOH)_2 \cdot 2H_2O$, Kanto

26 Chemical Co., Inc.) was used. A stock solution of containing bromine at 10 mg mL^{-1}

27 was prepared by dissolving ammonium bromide (NH_4Br, Sigma Aldrich, USA) in

28 ultrapure water. From these stock solutions, 0, 100, 500, 1000, 1500, 2000, 3000 and

29 4000 μg mL^{-1} sample solutions of carbon and bromine were prepared by diluting by

30 ultrapure water.

31   A multi-element solution was prepared from 1 mg mL^{-1} Be, P, Cu, Zn, As, Se, Cd,

32 Sb, I, W, Pt and Au standards (chemical analysis grade, Kanto Chemical Co., Inc.,

33 Tokyo, Japan) and 1 mg mL^{-1} B, S and Te standards (SPEX CertiPrep Inc., USA). The

34 concentrations of the elements in the multi-element solution were as follows: 0.1 μg

35 mL^{-1} Cu and B and 0.5 μg mL^{-1} Be, P, S, Zn, As, Se, Cd, Sb, Te, I, W, Pt and Au.

36   RbBr (Wako Pure Chemical Industries, Osaka, Japan) and CsI (Kanto Chemical Co.,

1   Inc.) were used for measuring plasma temperature. RbBr and CsI were dissolved in the

2   carbon and bromine sample solutions so that the Br and I concentrations were 0.1 μg

3   mL^{-1} and 0.1 μg mL^{-1}, respectively.

4

5   **2.2 ICP-MS**

6

7   ICP-MS measurements were performed with an HP4500 spectrometer (Agilent

8   Technologies, Tokyo, Japan). The instrumental operating parameters are listed in Table

9   1, and a schematic diagram of the analytical system is shown in Fig. 1. One hundred

10   microliters of a sample solution of carbon or bromine was injected into a Scott-type

11   spray chamber via a flow injection system. Ultrapure water or the multi-element

12   solution was introduced into an ultrasonic nebulizer (U-6000AT^{+}, CETAC Technologies,

13   Omaha, USA) coupled with a desolvation system (membrane desolvator, CETAC

14   Technologies, Omaha, USA) by means of a peristaltic pump (Minipuls 3, Gilson,

15   France) at a sample uptake rate of 0.5 mL min^{-1}. Aerosols from the spray chamber and

16   the ultrasonic nebulizer were merged and then introduced into the ICP-MS.

17

18   **2.3 Calculation of signal enhancement ratios**

19

20   To determine the signal enhancements due to co-existing carbon, we introduced

21   ultrapure water or a sample solution of carbon into the ICP by means of the concentric

22   nebulizer while the multi-element solution was introduced into the ICP by means of the

23   ultrasonic nebulizer. The intensities of the ^{9}Be, ^{11}B, ^{40}Ar^{12}C, ^{31}P, ^{34}S, ^{65}Cu, ^{66}Zn, ^{75}As,

24   ^{77}Se, ^{81}Br^{1}H, ^{111}Cd, ^{121}Sb, ^{125}Te, ^{127}I, ^{182}W, ^{195}Pt and ^{197}Au signals were measured in

25   time-resolved analysis mode. Signal enhancement ratios were calculated by dividing the

26   area of each analyte peak in the presence of carbon by the area in the presence of

27   ultrapure water.

28

29   **2.4 Measurement of plasma ionization temperature**

30

31   For determination of the plasma ionization temperature (T_i), a carbon sample solution

32   containing RbBr or a bromine sample solution containing CsI was introduced into the

33   ICP-MS by means of the flow injection system. The ratio of the intensities of the Br^{+}

34   and Rb^{+} signals and the ratios of the intensities of the I^{+} and Cs^{+} signals were used to

35   calculate T_i from eqn (2):

36

1　　$$\frac{\alpha}{1-\alpha} = \frac{n_i}{n_a} = \frac{1}{n_e} \times \frac{(2\pi m k T_i)^{\frac{3}{2}}}{h^3} \frac{2Z_i}{Z_a} \exp\left[-\frac{E_i}{kT_i}\right] \tag{2}$$

2

3　where α is the ionization degree; n_i, n_a and n_e are the number densities (m⁻³) of ions,

4　atoms and electrons, respectively; m is the mass of the electron (kg); k is the Boltzmann

5　constant (J K⁻¹); h is the Planck constant (K s), Z_i and Z_a are the ion and atom partition

6　functions; and E_i is the ionization energy (J).[23,24] In this equation, Br^+/Rb^+ and I^+/Cs^+

7　can be substituted for α in chapter 3.4. For n_e a typical number density of 1.0×10^{15} cm⁻³

8　was used.[25]

9

10　**3 Results and discussion**

11

12　**3.1 Effects of co-existing carbon on analyte signals**

13

14　Two typical signal intensity profiles are shown in Fig. 2 for an experiment in which the

15　multi-element solution was continuously introduced into the ICP via ultrasonic

16　nebulizer, so that the analyte signals were observed continuously during the

17　measurement. A sample solution of carbon was also introduced into the ICP via

18　concentric nebulizer, and the carbon and analyte signals were simultaneously observed

19　in time-resolved analysis mode. The intensity of the Cu signal was constant even when

20　the sample solution of carbon was introduced into the ICP (Fig. 2a); that is, the Cu

21　signal was not enhanced by co-existing carbon. In contrast, the As signal was enhanced

22　by co-existing carbon (Fig. 2b). The signal enhancement ratios of B, P, S, As, Se and I

23　as a function of carbon concentration are shown in Fig. 3. Signal enhancement was

24　observed for B, P, S, As, Se and I, and the magnitude of the enhancement increased with

25　increasing carbon concentration. The signal enhancement ratios of B, P, S, As, Se and I

26　at a carbon concentration of 4000 μg mL⁻¹ were 116, 119, 113, 132, 137 and 144%,

27　respectively. Because in this study the sample introduction efficiency was the same with

28　and without carbon, we attributed the signal enhancements to CT, the relative bond

29　energies of the analyte and carbon oxides and a change in the plasma temperature. The

30　ionization energies of B, P, S, As, Se and I, the elements for which signal enhancements

31　were observed, are 8.29, 10.48, 10.36, 9.81, 9.75 and 10.45 eV, respectively. It has been

32　reported that CT occurs when the difference between the ionization energy of C (11.26

33　eV) or CH (10.64 eV) and that of the analyte is less than 2 eV.[26] Because the differences

34　in ionization energy between B and C and between B and CH exceed 2 eV, we assumed

35　that CT was not responsible for the signal enhancement observed for B.

3.2 Effect of co-existing bromine on analyte signals

To examine the influence of CT, we conducted signal enhancement experiments with sample solutions of bromine, which has an ionization energy similar to that of carbon and should therefore result in signal enhancement in the same way that carbon does. We found that no signal enhancement was observed for B, P, S, As, Se and I at any of the tested bromine concentration (Fig. 4). The signal enhancement ratios at a bromine concentration of 4000 μg mL^{-1} were 99, 100, 101, 101, 101 and 100%, respectively. Therefore, some difference between carbon and bromine must be invoked to explain their different effects on signal intensity. One possibility is the difference between the bond energies of the oxides of carbon and bromine, which differ substantially (1076 and 235 kJ mol^{-1}, respectively).[27]

3.3 Effects of bond energies of analyte, carbon and bromine oxides

As stated above, signal enhancements due to co-existing carbon have been attributed to CT, as shown in eqn (1). As illustrated in Fig. 5, the CT mechanism is believed to involve transfer of the energy of C$^+$-species to the analyte atoms in the plasma, which results in an increase in the ionization degree (α) of the analyte atoms. In addition, because the bond energy of carbon oxide is high relative to the bond energies of the analyte oxides, the analyte oxides are reduced in the plasma, and the C is oxidized. This process increases the atomization ratio (β) of the analyte oxides, thus increasing the number of analyte atoms and enhancing their signals. In contrast, bromine oxide has a low bond energy and thus has difficulty reducing the analyte oxides. Therefore, no signal enhancement due to co-existing bromine is observed. The bond energy of boron oxide is quite high (809 kJ mol^{-1}), and thus B exists as its oxide, which is reported to be reduced by the introduction of carbon.[14] Boron oxide is reduced in the ICP while C is oxidized, and thus signal enhancement by co-existing carbon is observed, even though CT is unlikely (owing to the large difference in ionization energy between B and carbon species).

To determine the quantities of analyte oxides, we analyzed a 1 μg mL^{-1} multi-element solution by ICP-MS and calculated oxide production ratios using eqn (3):

$$\text{Oxide production ratio [\%]} = MO^+/M^+ \qquad (3)$$

1   where MO^+ is the analyte oxide ion count, and M^+ is the analyte ion count. It was

2   assumed that the ionization energies of MO and M are the same. The bond energies of

3   selected analyte oxides[27] and the theoretical values of their ionization degrees[25] in the

4   ICP are listed in Table 2, along with the experimentally observed oxide production

5   ratios. The oxide production ratio of B (4.219%) was the highest ratio observed for any

6   of the analytes we tested. When we plotted the oxide production ratios of these nine

7   elements as a function of the bond energies of the corresponding oxides (Fig. 6), a linear

8   relationship was observed, with tungsten oxide as an outlier. The bond energy of

9   tungsten oxide is 832 kJ mol^{-1}, which is close to that of boron oxide. However, because

10   almost all the W (93.64%) was ionized in the plasma, the oxide production ratio of W

11   was substantially lower than that of B, despite the similar oxide bond energies of the

12   two elements.

13

14   **3.4 Plasma temperature**

15

16   We also used a sample solution of carbon or bromine containing RbBr or CsI,

17   respectively, to measure the plasma temperature. The ionization energies of Rb and Cs

18   are 4.18 and 3.89 eV, respectively, and Rb and Cs are completely ionized in the plasma.

19   In contrast, the ionization energies of Br and I are 11.81 and 10.45 eV, respectively; thus

20   only portions of Br and I are ionized in the plasma. Additionally, the second ionization

21   energies of Rb, Br, Cs and I are higher than the ionization energy of Ar (16.7 eV).

22   Therefore, doubly charged Rb, Br, Cs and I ions are produced to a very limited extent.

23   Consequently, the Br^+/Rb^+ and I^+/Cs^+ ratios can be substituted for the ionization degree

24   (α) in eqn (2). To measure plasma temperature, we used a RbBr solution for the sample

25   solution of carbon, because the I signal is enhanced by co-existing carbon.[9,28] The

26   signals of ^{85}Rb, ^{79}Br, ^{133}Cs and ^{127}I were used to calculate the plasma temperature from

27   eqn (2). Plasma temperature decreased with increasing carbon and bromine

28   concentrations (Fig. 7); the 4000 μg mL^{-1} sample solutions of carbon and bromine

29   reduced the plasma temperature from 6860 to 6750 K and from 6990 to 6930 K,

30   respectively. The ionization degree can be expected to decrease with decreasing the

31   plasma temperature. For example, the ionization degree of As is influenced from 24% to

32   21% in the case of carbon and from 18% to 15% in the case of bromine. The decrease of

33   ionization would decrease rather than enhance signal intensity.

34

35   **3.5 Mechanism of the signal enhancement**

36

1   Table 2 summarizes the ionization energies, analyte oxide bond energies[27] and
2   ionization degrees[25] of all of the analytes evaluated in this study. The intensities of the P,
3   I, S, As, Se and B signals were enhanced by co-existing carbon, whereas no signal
4   enhancement was observed for Zn, Be, Au, Te, Pt, Cd, Sb, W and Cu. Our results
5   suggest that signal enhancement due to co-existing carbon can be observed for elements
6   whose ionization degrees were less than 60% and whose MO bond energies were higher
7   than 450 kJ mol^{-1}. Iodine was an exception. We suggest that the mechanism of the signal
8   enhancement was reduction of the analyte oxides by carbon. Iodine oxide has a low
9   bond energy (240 kJ mol^{-1}), but the ionization energy of I (10.45 eV) is close to that of
10 CH (10.64 eV) and that of C (11.26 eV). Therefore, we attributed the enhancement of
11 the I signal to a CT reaction with C$^+$-species. The signal enhancement due to co-existing
12 carbon has been reported to increase with increasing nitric acid concentration.[6] We also
13 confirmed the signal enhancement increased with decreasing pH as shown in Fig. 8.
14 Therefore, it was found that the signal intensity of I is enhanced more effectively by
15 CH$^+$ than by C$^+$. As the C$^+$-species in CT reactions shown in eqn (1), CH$^+$ involved to
16 enhance the signal more effectively than C$^+$ did. We considered that the effect of CT
17 could not be eliminated, because enhancement of the I signal by co-existing carbon was
18 observed. Consequently, we concluded that both reduction of analyte oxides by carbon
19 and CT were the main causes of signal enhancement due to co-existing carbon.

20

21 **4 Conclusion**

22

23 In this study, we compared the signal enhancement effects of co-existing carbon and
24 co-existing bromine. We found that co-existing bromine did not enhance the signals of
25 any of the tested analytes, even though its ionization energy is similar to that of carbon.
26 To explain this finding, we focused on the bond energies of carbon and bromine oxides.
27 Carbon oxide has a high bond energy. Therefore, we suggest that the signal
28 enhancement effects of carbon were due to oxidation of carbon by the analyte oxides,
29 which were in turn reduced to the corresponding analyte atoms; this process resulted in
30 an increase in the atomization ratio (β) of the analyte oxides. However, signal
31 enhancement was observed for I, even though the bond energy of iodine oxide is less
32 than 450 kJ mol^{-1}. We suggest that the reason for this is that the ionization energy of I
33 (10.45 eV) is close to that of CH (10.64 eV) and therefore that CT from CH$^+$ to I
34 occurred readily. Our results indicate that CT cannot be eliminated as an explanation for
35 signal enhancement by co-existing carbon. We suggest that both reduction of analyte
36 oxides and CT contribute to the signal enhancement effects of co-existing carbon. In

summary, we found that signal enhancements were observed for analytes that were less than 60% ionized in the ICP and whose analyte oxide bond energies were higher than 450 kJ mol^{-1}.

Acknowledgements

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1   Table 1   ICP-MS operating conditions

2

Agilent HP4500 ICP-MS	
rf power	1400 W
Coolant gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate (concentric nebulizer)	0.65 L min^{-1}
Sample uptake rate (concentric nebulizer)	0.5 mL min^{-1}
Carrier gas flow rate (ultrasonic nebulizer)	0.60 L min^{-1}
Sample uptake rate (ultrasonic nebulizer)	0.5 mL min^{-1}
Chamber	Scott type
Sampling cone	orifice diameter 1 mm Ni
Skimmer cone	orifice diameter 0.4 mm Ni
Sampling depth	7.5 mm from top of the load coil
Dwell time per isotope	0.1 sec
Isotopes measured	^{9}Be, ^{11}B, ^{40}Ar^{12}C, ^{31}P, ^{34}S, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se or ^{82}Se, ^{79}Br, ^{81}Br^{1}H, ^{85}Rb, ^{111}Cd, ^{121}Sb, ^{125}Te, ^{127}I, ^{133}Cs, ^{182}W, ^{195}Pt, ^{197}Au

3

4

1 Table 2 Oxide production ratios, ionization energies, analyte oxide (MO) bond

2 energies and ionization degrees in the ICP of all measured analytes

3

	Element	Oxide production ratio [%]	Ionization energy[eV]	Bond energy of MO [kJ mol^{-1}]	Degree of ionization in ICP [%]
Enhanced	P	0.423	10.48	589	33.11
	I	-*	10.45	240	29.85
	S	0.311	10.36	517	14.3
	As	0.042	9.81	484	51.64
	Se	0.047	9.75	469	33.32
	B	4.219	8.29	809	58.06
Not enhanced	Zn	-*	9.39	226	75.33
	Be	0.068	9.32	437	74.98
	Au	-*	9.12	223	50.74
	Te	0.009	9.01	377	66.38
	Pt	-*	9.00	391	62.43
	Cd	-*	8.99	236	85.03
	Sb	0.023	8.46	434	79.98
	W	0.121	7.98	832	93.64
	Cu	-*	7.73	280	89.25

4 * These are not measured.

5

1   Figure captions

2

3   Fig. 1   Schematic diagram of the sample introduction system.

4

5   Fig. 2   Signal intensity profiles of (a) ^{63}Cu and (b) ^{75}As when the sample solution of

6   carbon was introduced.

7

8   Fig. 3   Dependence of signal enhancement ratios of ^{11}B, ^{31}P, ^{34}S, ^{75}As, ^{77}Se and ^{127}I on

9   carbon concentration. Error bars indicate standard deviation (n=3).

10

11   Fig. 4   Dependence of signal enhancement ratios of ^{11}B, ^{31}P, ^{34}S, ^{75}As, ^{77}Se and ^{127}I on

12   bromine concentration. Error bars indicate standard deviation (n=3).

13

14   Fig. 5   Schematic diagram of signal enhancement by co-existing carbon. Positively

15   charged carbon species (C$^+$-species) react with the analyte atom (M), and the degree of

16   ionization (α) of the analyte increases. Carbon is oxidized by the analyte oxide (MO),

17   and the analyte oxide is reduced to the analyte atom. This process increases the

18   atomization ratio (β) of the analyte oxide. In contrast, bromine is not oxidized by the

19   analyte oxide.

20

21   Fig. 6   Oxide production ratio as a function of analyte oxide (MO) bond energy.

22

23   Fig. 7   Effect of carbon and bromine concentration on plasma ionization temperature,

24   as measured by using sample solutions of containing RbBr (C) and CsI (Br).

25

26   Fig. 8   Signal enhancement ratios of ^{75}As, ^{82}Se and ^{31}P as a function of carbon

27   concentration for difference pH: (□) pH 2; (Δ) pH 4; (◊) pH 6; and pH 8 (○).

28   Error bars indicate standard deviation (n=3). Oxalic acid was used for a carbon

29   source and pH adjustment was conducted by adding HNO_3 or NH_4OH.

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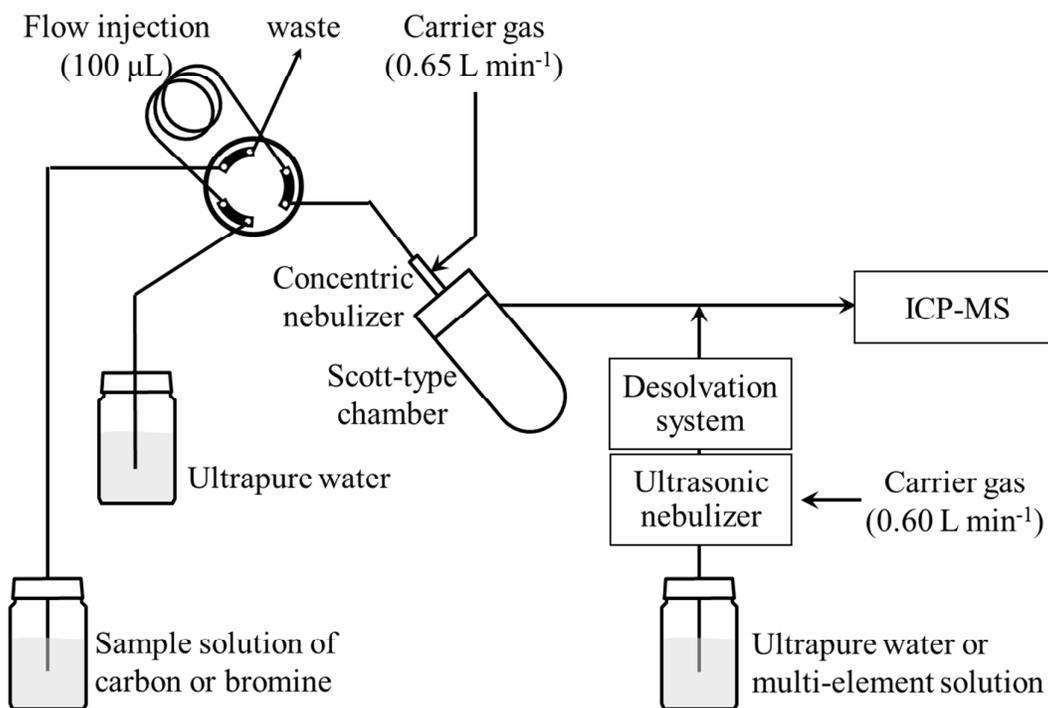
3   Fig. 1   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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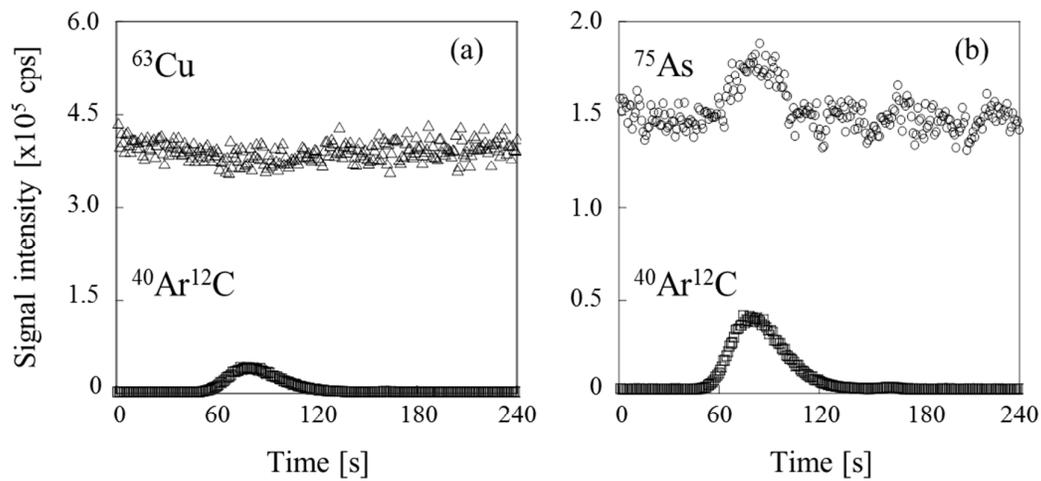
3   Fig. 2   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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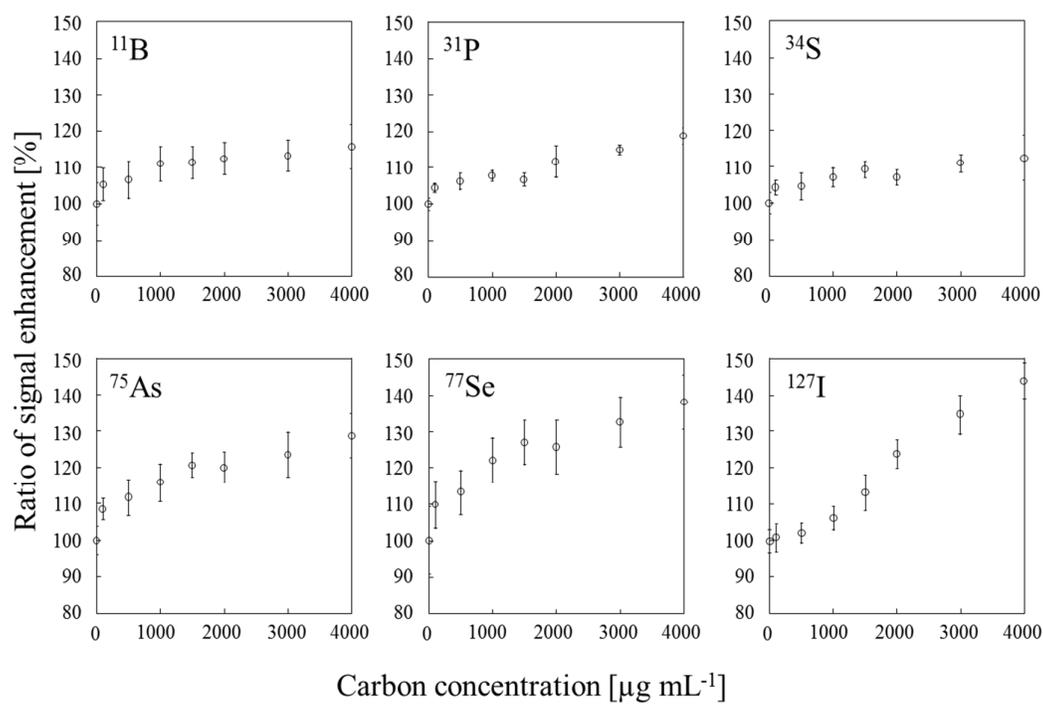
Fig. 3   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*
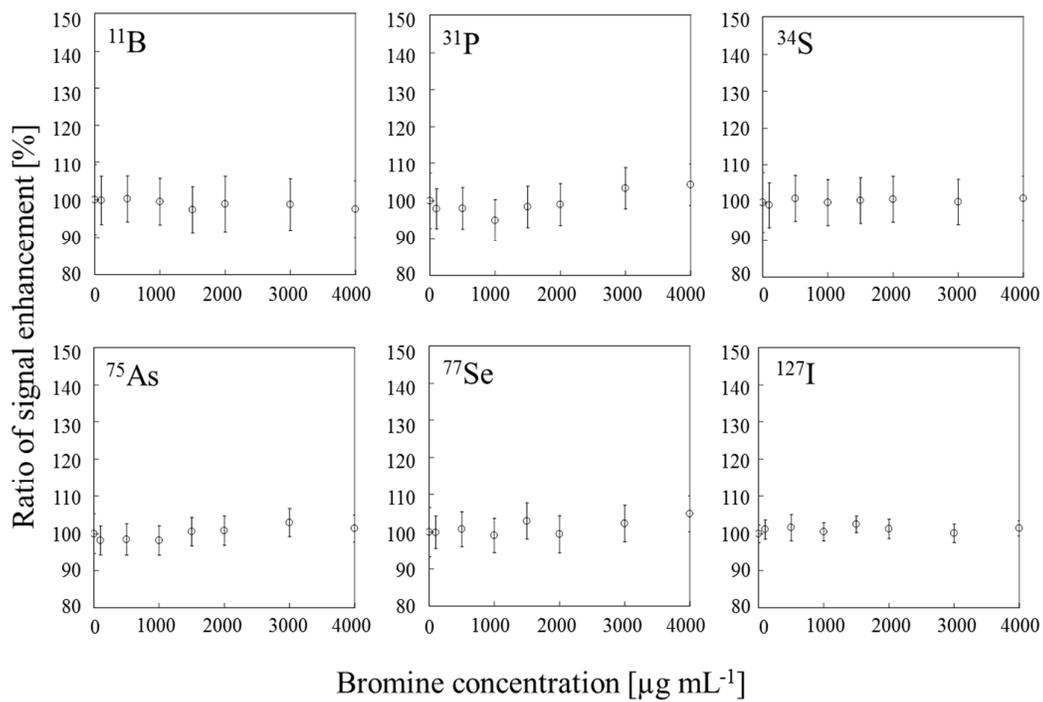
Fig. 4   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*
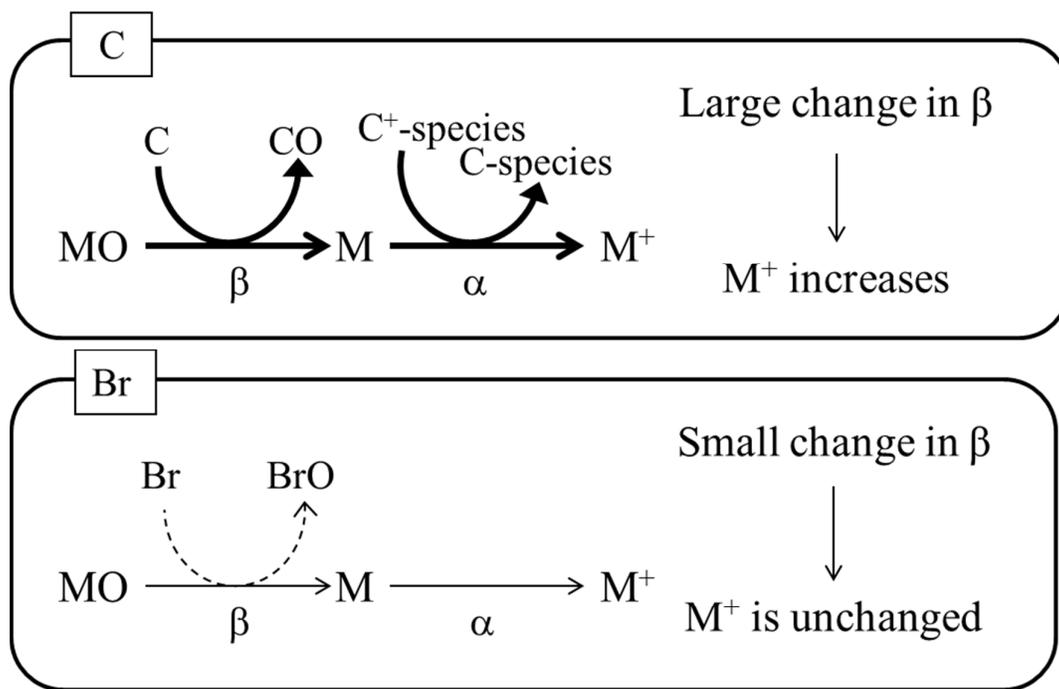
Fig. 5 *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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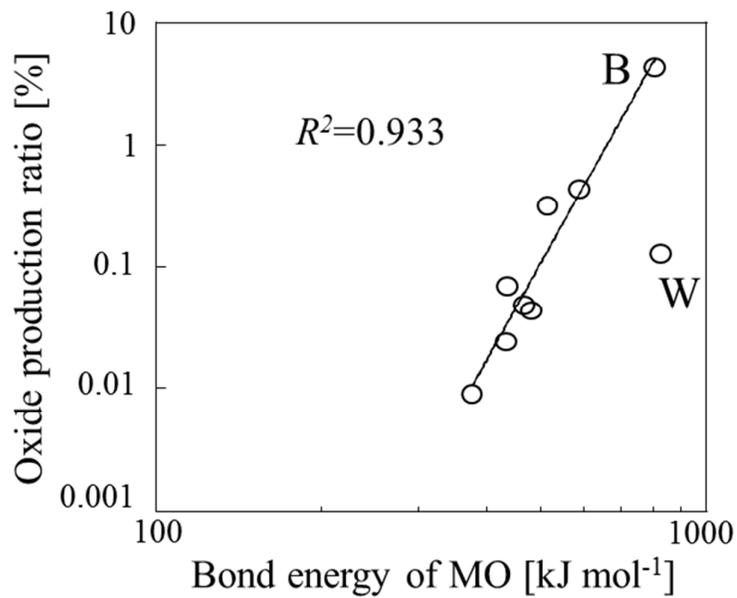
3   Fig. 6   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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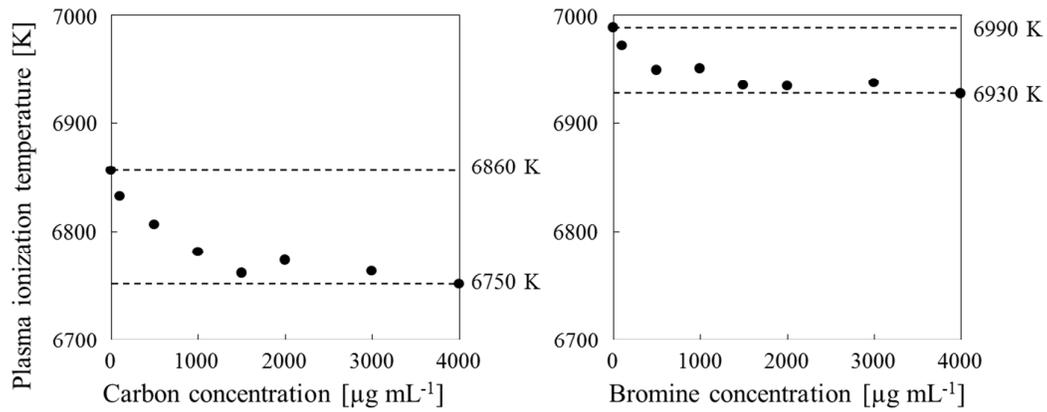
3 Fig. 7 *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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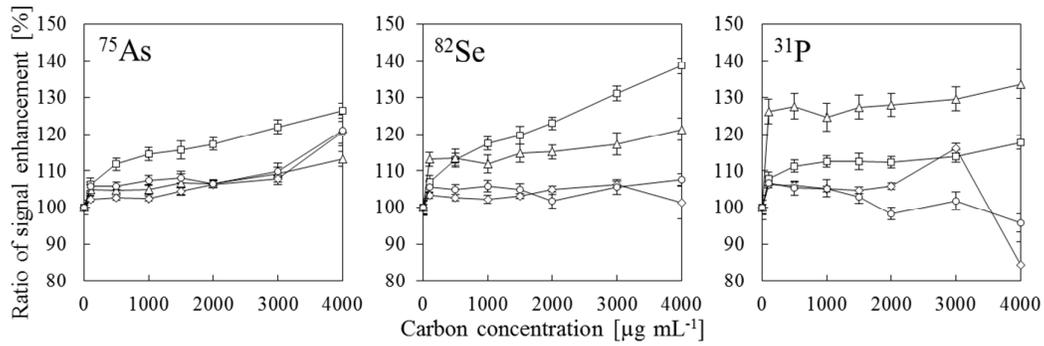
2   Fig. 8   *T. Nakazawa, D. Suzuki, H. Sakuma and N. Furuta*

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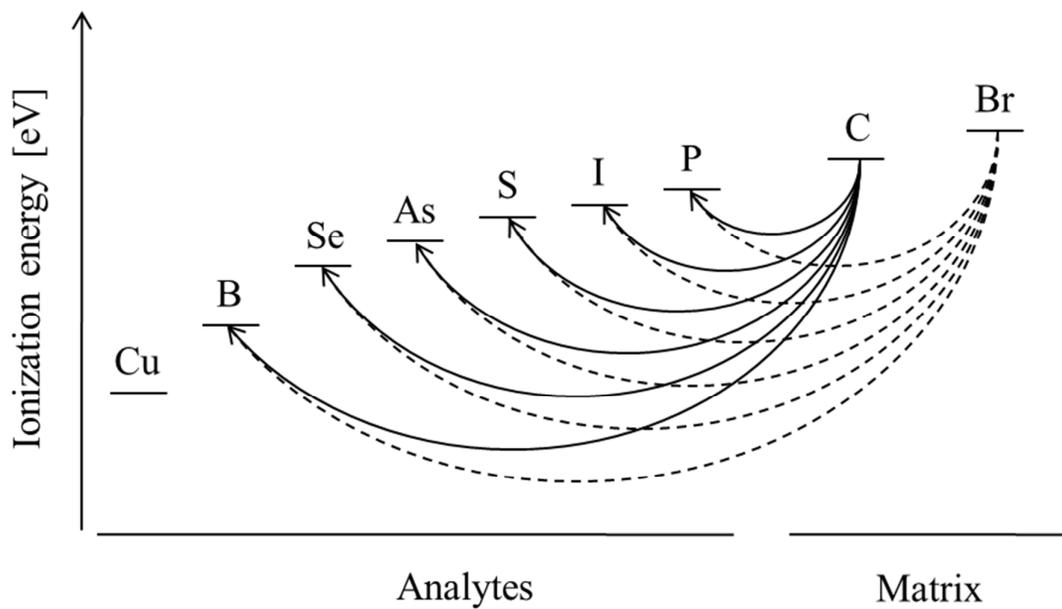
Co-existing bromine did not enhance the signals of analytes, even though the ionization energy is similar to carbon.