

# High Power Nitrogen Microwave Induced Plasma Atomic Emission Spectrometry Coupled with Hydride Generation Technique for the Determination of Several Elements

Akihiro Matsumoto<sup>a\*</sup> and Taketoshi Nakahara<sup>b</sup>

Contribution from:<sup>a</sup>Wakayama Industrial Technology Center, 60 Ogura, Wakayama 649-6261, Japan;  
<sup>b</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan.

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## Résumé

*Une source à plasma induit par micro-onde (MIP) à haute puissance dans une cavité de type Okamoto peut être maintenu dans l'hélium, l'azote et même l'air à pression atmosphérique. La cavité fut originalement développée et employée comme une autre source d'ionisation que le plasma d'argon à couplage inductif (ICP) pour la spectrométrie de masse (MS). Cette revue propose qu'il est faisable d'utiliser un plasma d'azote induit par micro-onde (N<sub>2</sub>-MIP) à haute puissance (1.0 kW) en forme d'anneau et maintenu à pression atmosphérique dans une cavité Okamoto comme nouvelle source d'excitation en spectrométrie d'émission atomique. Subséquemment, la combinaison de N<sub>2</sub>-MIP-AES à haute puissance avec la méthode de génération d'hydrure en flux continu est présentée pour des déterminations mono-élémentaires (arsenic, sélénium, antimoine, tellurium, bismuth, étain et plomb) et multi-élémentaires (arsenic & antimoine, bismuth & tellurium, arsenic, antimoine & bismuth, et arsenic, antimoine, bismuth & sélénium). Après une étude d'interférences, la présente méthode a été appliquée aux déterminations mono- et multi-élémentaires de concentrations de traces des éléments mentionnés ci-haut formant des hydrures dans plusieurs matériaux de référence d'acier. Les résultats obtenus par cette méthode étaient en bon accord avec les valeurs certifiées.*

## Abstract

*A high power microwave induced plasma (MIP) source produced by using an Okamoto cavity can be sustained by He, N<sub>2</sub> and even air at atmospheric pressure. The cavity was originally developed and employed to produce an alternative analytical ionization source to argon inductively coupled plasma (ICP) for mass spectrometry (MS). This review introduces the feasibility of using an annular-shaped high power (1.0 kW) nitrogen microwave induced plasma (N<sub>2</sub>-MIP), sustained at atmospheric pressure by the Okamoto cavity, as a new excitation source for atomic emission spectrometry (AES). Subsequently, the combination of high power N<sub>2</sub>-MIP-AES with the continuous-flow hydride generation method for single (arsenic, selenium, antimony, tellurium, bismuth, tin and lead) and multi- (arsenic & antimony, bismuth & tellurium, arsenic, antimony & bismuth, and arsenic, antimony, bismuth & selenium) element determination has been presented. After the interference study, the present method has been applied to the single and multi-element determination of trace concentrations of the above-mentioned hydride-forming elements in several reference materials of steels. The results obtained by this method were in good agreement with their certified values.*

**Keywords:** High power nitrogen microwave induced plasma, Okamoto cavity, atomic emission spectrometry, hydride generation method, simultaneous multi-element determination, arsenic, selenium, antimony, tellurium, bismuth, tin, lead, steels.

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\* Author to whom correspondence should be addressed:  
amats@wakayama-kg.go.jp

## Introduction

For the determination of trace elements, atomic absorption spectrometry (AAS), both with flames and electrothermal atomizers, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are probably the most powerful techniques in analytical atomic spectrometry, and they have been widely used in particular for a number of practical samples. The last two methods also have the ability to make highly sensitive, precise and accurate multi-element measurements (1-5). However, the use of Ar-ICP-MS could not make the determination of the elements such as  $^{52}\text{Cr}^+$ ,  $^{56}\text{Fe}^+$ ,  $^{75}\text{As}^+$ ,  $^{78}\text{Se}^+$  and  $^{80}\text{Se}^+$  possible, except when using modern instruments equipped with collision cells (6,7) and dynamic reaction cells (8-10). Moreover, the running costs of the Ar-ICP become higher.

On the other hand, several alternatives to ICP systems have been proposed; one of these alternative plasma sources is a microwave induced plasma (MIP). In 1976, Beenakker (11) introduced a  $\text{TM}_{010}$  cavity with which Ar- and He- MIPs could be generated at atmospheric pressure. Since then, the MIP generated by using the Beenakker cavity has found many applications (11-18). This source has the advantages of low cost, low gas consumption and ease of use (5). Also, different types of low power MIPs (up to 500 W), including ones produced by use of the surfatron (12,19) and the microwave plasma torch (MPT) (20), have been developed. Then, Carnahan *et al.* (21-23) developed a high power (1600 W) KiP-MIP. However, these MIPs have a low tolerance for the direct and continuous introduction of aqueous samples. In order to overcome these limitations, Okamoto (24,25) developed a new cavity-torch arrangement that is able to produce a doughnut-shaped high power (1.0 kW) nitrogen microwave induced plasma ( $\text{N}_2$ -MIP) at atmospheric pressure, just the same as Ar-ICP. This  $\text{N}_2$ -MIP enables the direct introduction of sample aerosols into the center of plasma. The Okamoto cavity was originally developed and subsequently used to produce an alternative analytical ionization source to argon ICP-MS. When  $\text{N}_2$  is used as the plasma sustaining gas, interferences due to Ar-associated species, such as  $^{40}\text{Ar}^{12}\text{C}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^+$ ,  $^{40}\text{Ar}^{35}\text{Cl}^+$  and  $^{40}\text{Ar}_2^+$ , do not occur in the MS, and thus the determination of  $^{52}\text{Cr}^+$ ,  $^{56}\text{Fe}^+$ ,  $^{75}\text{As}^+$  and  $^{80}\text{Se}^+$  could be possible using a high power  $\text{N}_2$ -MIP-MS. Moreover, the running costs become lower than those

of the Ar-ICP. Recently, the excitation temperature and the electron density of high power  $\text{N}_2$ -MIP were investigated (26-28). Also, a few applications of high power  $\text{N}_2$ -MIP as an excitation source for AES were performed for the determination of trace elements in a variety of real samples (29-44).

The analytical capabilities of MIPs depend strongly on the cavities used (45,46). The basic characteristics, such as the electron density and the excitation temperature, of He-, Ar- and  $\text{N}_2$ -MIP (36,47,48) as compared with those of He- and Ar-ICP (30,49) were reported. Okamoto *et al.* (26) reported the electron density and the excitation temperature of  $\text{N}_2$ -MIP were  $3 \times 10^{13} \text{ cm}^{-3}$  and 5500 K, respectively. On the other hand, those of the Ar-ICP were  $1 \times 10^{15} \text{ cm}^{-3}$  and 7500 K, respectively. Although the  $\text{N}_2$ -MIP has a lower excitation temperature and lower electron density than the Ar-ICP, the  $\text{N}_2$ -MIP is mentioned as a similarly powerful plasma source to Ar-ICP. Moreover, for practical applications such as an analytical ionization or excitation source, investigation of matrix effects in the high power  $\text{N}_2$ -MIP is significantly important. Wagatsuma *et al.* (28) reported the excitation temperature and the electron density of high power  $\text{N}_2$ -MIP when the solution contains a matrix such as Na, Ca and nitric acid.

This review introduces the annular-shaped high power  $\text{N}_2$ -MIP-AES with the continuous-flow hydride generation method, which was described for the single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead. Moreover, the same technique has been extended for the multi-element determination of two (arsenic & antimony, bismuth & tellurium), three (arsenic, antimony and bismuth), and four elements (arsenic, antimony, bismuth and selenium). After studying the effects of diverse elements, the present method has been successfully applied to the determination of trace concentrations of the above-mentioned hydride-forming elements in steels.

## Experimental

### *Instrumentation and apparatus*

A schematic diagram of the experimental apparatus is shown in Figure 1, and the major instruments used in this work are listed in Table 1. Microwave power is transferred from a magnetron (2.45 GHz, 1.0 kW) of a Nippon Kousyuhua MKN-103-3S microwave power generator to the torch through a uniline, directional

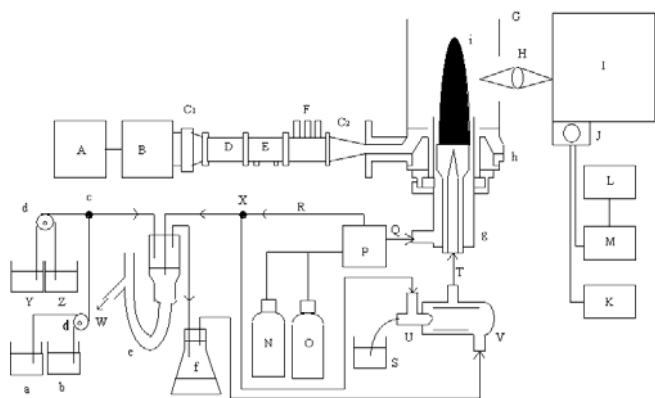


Figure 1. Schematic diagram of high power  $N_2$ -MIP-AES system. A: microwave power supply, B: microwave generator,  $C_1$ ,  $C_2$ : tapered wave guide, D: uniline, E: direction coupler, F: three-stub tuner, G: copper pipe, H: lens, I: monochromator, J: photomultiplier, K: high-voltage power supply, L: printer, M: computer, N: nitrogen tank, O: argon tank, P: gas controller, Q: plasma gas, R: carrier gas, S: sample solution for nebulization, T: carrier gas for sample aerosol or hydride, U: nebulizer, V: nebulizer chamber, W: waste, X: three-way stopcock, Y: sample solution for hydride generation, Z:  $NaBH_4$  solution, a: pre-reduction solution for analyte elements, b: interference-releasing solution for iron, c: mixing joint, d: peristaltic pump, e: gas-liquid separator, f: drying flask, g: discharge tube (plasma torch), h: cavity, i: plasma.

coupler, three-stub tuner, tapered waveguide and an Okamoto cavity. An annular-shaped plasma is formed above the quartz torch. The computer-controlled sequential spectrometer used in this work was a part of a Nippon Jarrell-Ash ICAP-575 II inductively coupled plasma emission spectrometer. A high power  $N_2$ -MIP source, together with a magnetron, was mounted on a laboratory-made optical rail for x-y-z direction adjustments. For hydride generation, in particular, a drying flask filled with concentrated sulfuric acid as a desiccant was installed between a laboratory-made gas-liquid phase separator and a nebulization chamber in order to remove the water vapor produced during hydride generation. This is shown in Figure 1.

#### General procedure

For hydride generation, an acidified sample solution or a standard solution of arsenic, selenium, antimony, tellurium, bismuth, tin and lead, and the sodium tetrahydroborate (III) solution were continuously introduced into a gas-liquid phase separator (e in Figure 1) using a peristaltic pump (d in Figure 1). The generated arsenic, selenium, antimony, tellurium, bismuth, tin and lead hydrides, after being passed through a drying flask

Table 1. Experimental instrumentation for high power  $N_2$ -MIP-AES

Component	Model	Manufacturer
Microwave generator	MKN-103-3S	Nippon Kousyuha
Microwave cavity	Okamoto cavity	Hitachi
MIP torch	300-8352	Hitachi
Sequential spectrometer	Part of ICAP-575	Nippon Jarrell-Ash
Photomultipliers	R427 and R550	Hamamatsu Photonics
Personal computer	PC-9821	NEC
Peristaltic pump	MP-3	Tokyo Rikakikai

(f in Figure 1) to remove the water vapor, are swept into the high power  $N_2$ -MIP source (i in Figure 1) through the drain outlet of the conventional nebulizer chamber (V in Figure 1) by a stream of nitrogen carrier gas. For a conventional solution nebulization method, either a sample solution aerosol or a standard solution aerosol of arsenic, selenium, antimony, tellurium, bismuth, tin and lead was nebulized directly into the high power  $N_2$ -MIP source through the conventional nebulizer chamber.

## Results and Discussion

### Single-element determination by high power $N_2$ -MIP-AES coupled with hydride generation technique

*Determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by high power  $N_2$ -MIP-AES coupled with hydride generation technique*

*Optimization of experimental conditions and analytical performance*

The optimized experimental conditions of the conventional solution nebulization and hydride generation methods used are shown in Table 2. Under the optimized operating conditions, the detection limits for arsenic, selenium, antimony, tellurium, bismuth, tin and lead, which were extrapolated from the linear calibration graphs and defined as the concentration of the analyte that would produced a net signal (i.e., background-corrected line intensity) equal to three times the standard deviation of the background emission intensity, are shown in Table 3. As a result, the sensitivity with the use of the hydride

Table 2. Optimized operating conditions for the single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by high power N<sub>2</sub>-MIP-AES with hydride generation

Element	As	Se	Sb	Te	Bi	Sn	Pb
Plasma							
Wavelength (nm)	As I 228.812	Se I 196.026	Sb I 231.147	Te I 214.281	Bi I 223.061	Sn I 235.485	Pb I 368.347
Microwave forward power (W)	1000 (1000) <sup>a</sup>	1000 (1000)	1000 (1000)	1000 (1000)	1000 (1000)	1000 (1000)	1000 (700)
Plasma gas flow rate (L/min)	11 (14)	11 (14)	16 (12)	18 (13)	11 (17)	11 (13)	12 (14)
Carrier gas flow rate (L/min)	0.5 (0.6)	0.4 (0.6)	0.2 (0.6)	0.2 (0.95)	0.5 (1.3)	0.3 (1.3)	0.3 (1.0)
Vertical observation position (mm above the top of the cavity)	7 (13)	2 (3)	5 (4)	6 (5)	4 (4)	10 (4)	3 (4)
Horizontal observation position (mm)	0 (centered) (0, centered)	0 (centered) (0, centered)	0 (centered) (0, centered)	0 (centered) (0, centered)	0 (centered) (0, centered)	0 (centered) (0, centered)	0 (centered) (0, centered)
Hydride generation							
NaBH <sub>4</sub> concentration (%)	0.5	0.4	1.0	2.0	0.4	0.4	0.3
NaOH concentration (%)	0.5	0.4	0.5	1.0	0.4	0.4	0.3
Sample acidity (M in HCl)	1.0	1.0	1.0	2.0	1.0	1.0	1.0
Sample solution flow rate (mL/min)	12.2	12.0	10.8	11.0	8.2	3.4	8.4
NaBH <sub>4</sub> solution flow rate (mL/min)	10.8	11.0	11.6	10.4	11.3	3.2	5.7
Reference	34	34	36	35	41	43	44

<sup>a</sup>Conventional solution nebulizationTable 3. Analytical figures of merit for the single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by high power N<sub>2</sub>-MIP-AES with hydride generation

	Analyte						
	As	Se	Sb	Te	Bi	Sn	Pb
Linear dynamic range	5 - 10,000 ng/mL (1 - 1,000 µg/mL) <sup>a</sup>	1 - 5,000 ng/mL (2 - 1,000 µg/mL)	5 - 10,000 ng/mL (0.5 - 500 µg/mL)	50 - 50,000 ng/mL (0.5 - 500 µg/mL)	30 - 30,000 ng/mL (1 - 1,000 µg/mL)	300 - 30,000 ng/mL (3 - 1,000 µg/mL)	100 - 30,000 ng/mL (1 - 1,000 µg/mL)
Detection limit (3σ)	2.99 ng/mL (450 ng/mL)	0.86 ng/mL (1090 ng/mL)	1.87 ng/mL (510 ng/mL)	15 ng/mL (740 ng/mL)	102 ng/mL (3040 ng/mL)	52.3 ng/mL (1190 ng/mL)	35.2 ng/mL (160 ng/mL)
Correlation coefficient	0.998 (0.999)	0.999 (0.997)	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)
Reference	34	34	36	35	41	43	44

<sup>a</sup>Conventional solution nebulization

generation method for these elements is found to be greatly improved when compared with a conventional solution nebulization method. For the other methods by hydride generation-ICP-AES (50-55), ICP-MS (56-60) and AAS (61-64), the detection limits for arsenic, selenium, antimony, tellurium, bismuth, tin and lead are

shown in Table 4. The detection limits of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by the present high power N<sub>2</sub>-MIP-AES method with hydride generation are somewhat poorer than these obtained by the other methods (50-64), as shown in Table 4.

Table 4. Comparison of detection limit for arsenic, selenium, antimony, tellurium, bismuth, tin and lead by the presented MIP-AES, ICP-AES/MS and AAS with hydride generation

	Detection limit of analyte (ng/mL)							Reference
	As	Se	Sb	Te	Bi	Sn	Pb	
MIP-AES	2.99	0.86	1.87	15	102	52.3	35.2	34-36,41,43,44
ICP-AES	0.1	0.03	0.20	1.0	0.06	0.2	1.0	50-55
ICP-MS	0.007	0.01	0.005	0.027	0.02	0.002	0.002	56-60
AAS	0.006	0.01	0.14	0.2	0.025	0.025	1.5	61-64

#### Pre-reduction and pre-oxidation steps

Generally, though bismuth and tin exist only in the trivalent and tetravalent states, respectively, under an acidic condition, both arsenic and antimony exist in the trivalent and pentavalent states. Also, both selenium and tellurium exist in the tetravalent and hexavalent states. The generation efficiencies of their hydrides from the various oxidation states are different in the hydride generation technique (65-69). As (III), Sb (III), Se (IV) and Te (IV) solution gave much larger emission intensities than the same concentrations of As (V), Sb (V), Se (VI) and Te (VI), i.e., the ratios of intensities obtained from As (V), Sb (V), Se (VI) and Te (VI) to those from As (III), Sb (III), Se (IV) and Te (IV) were approximately 0.51, 0.15, 0.01 and 0.30, respectively, under the experimental conditions in Refs. 34-36, 41, 43 and 44. Therefore, their pentavalent and hexavalent states must be reduced to the corresponding trivalent and tetravalent states prior to hydride generation for the determination of total arsenic, antimony, selenium and tellurium [i.e., As (III) + As (V), Sb (III) + Sb (V), Se (IV) + Se (VI) and Te (IV) + Te (VI)]. Of the several pre-reductants investigated, potassium iodide (34) and L-cysteine (36) were found to be the most preferable to reduce arsenic and antimony prior to hydride generation, respectively. Also, a heating procedure in 5 M hydrochloric acid at 80°C for 20 min (34) and 6 M hydrochloric acid at 80°C for 30 min (35) was very effective in the pre-reduction of selenium and tellurium, respectively. Potassium iodide (50,70,71), L-cysteine (72-74) and hydrochloric acid (75-77) as pre-reductants have been used for arsenic, antimony, selenium and tellurium. In contrast, it is well known that a successful determination of lead requires the addition of an oxidizing agent prior to hydride generation (55,64,78,79). As a consequence of their evaluations, 1.0 % hydrogen peroxide was found to be the most effective reagent for the pre-oxidation of lead.

#### Effect of diverse elements

The determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by hydride generation-atomic spectrometry is well known to be susceptible to interferences from diverse elements (65-69). Under the experimental conditions used here, the effect of various other elements on the determination of these hydride-forming elements by the present hydride generation-high power N<sub>2</sub>-MIP-AES system was examined. The suppressing interferences from some elements are shown in Table 5. An interference is considered to have occurred when an emission intensity is changed by over 100 ± 5% from that of the analyte for each of arsenic, selenium, antimony, tellurium, bismuth, tin and lead. The relative intensity is defined in Table 5 as a ratio of the element emission intensity obtained in the presence of the foreign element or ion to that obtained when no element or ion was present in the analyte solution. As shown in Table 5, a number of elements interfered with the determination of these hydride-forming elements by the present technique. In particular, the presence of Co, Cu, Ni and BrO<sub>3</sub><sup>-</sup> gave rise to an interference when the present single-element determination method was used.

#### Single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead in steels

In order to demonstrate the effectiveness of the present method for practical analysis, some standard reference materials of steels were analyzed for arsenic, selenium, antimony, tellurium, bismuth, tin and lead using the hydride generation-high power N<sub>2</sub>-MIP-AES. The certified reference materials of steels issued by The Japan Iron and Steel Federation (JSS), National Institute of Standards and Technology (NIST), British Chemical Standard (BCS) and Nippon Yakin Kogyo Co. Ltd. (NAS) were used. It was expected that Fe (III), a major constituent of the steels, was likely to interfere with the single-element determination of arsenic, antimony, tellurium, bismuth, tin and lead by the proposed method, as shown in Table 5. However, the presence of Fe (II) showed little or no significant interference. In other words, this means that the Fe (III) in the sample solutions must be reduced to Fe (II) by an appropriate reductant and/or interference-releasing agent prior to hydride generation. Of the several interference-releasing agents examined, 1.0 and 0.1% L-ascorbic acid for arsenic and lead, 2% L-cysteine for antimony and tellurium, and 0.4 and 0.2% thiourea for bismuth and tin, were found to be the most

Table 5. Effect of diverse elements or ions on the single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead by high power N<sub>2</sub>-MIP-AES with hydride generation

Element or ion <sup>a</sup>	Relative intensity <sup>b</sup>						
	As	Se	Sb	Te	Bi	Sn	Pb
Ag	36	8.5	29	29	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>
As	100	58	40	38	93	85	88
Au	9.7	7.8	8.2	6.2	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>
Bi	-- <sup>c</sup>	80	54	3.1	100	57	90
Be	-- <sup>c</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>c</sup>	92	94	-- <sup>c</sup>
Cd	-- <sup>c</sup>	75	-- <sup>c</sup>	8.4	81	91	89
Co	35	44	21	15	85	89	86
Cr(III)	-- <sup>c</sup>	68	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	95	-- <sup>c</sup>
Cr(VI)	-- <sup>c</sup>	-- <sup>c</sup>	28	-- <sup>c</sup>	91	89	92
Cu	69	7.6	74	12	85	83	83
Cs	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	93	92	-- <sup>c</sup>
Fe(III)	78	-- <sup>c</sup>	38	24	81	85	87
Ga	86	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>
Ge	87	53	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	91	-- <sup>c</sup>
Hg	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	81	91	89
In	-- <sup>c</sup>	79	-- <sup>c</sup>	36	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>
Mn	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	82	94
Mo	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	67	87
Ni	24	11	7.9	12	86	77	86
P	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	85	-- <sup>d</sup>	-- <sup>c</sup>
Pb	-- <sup>c</sup>	57	-- <sup>c</sup>	-- <sup>c</sup>	85	84	100
Pd	17	8.5	0.9	5.8	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>
Sb	77	75	100	54	85	-- <sup>c</sup>	90
Se	64	100	30	11	88	77	92
Sn	-- <sup>c</sup>	85	-- <sup>c</sup>	26	90	100	91
Te	60	-- <sup>c</sup>	72	100	81	86	88
Ti	67	31	-- <sup>c</sup>	69	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>
V	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	83	77	84
W	-- <sup>d</sup>	-- <sup>d</sup>	41	-- <sup>c</sup>	75	-- <sup>d</sup>	87
Y	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	91	-- <sup>c</sup>
Zn	-- <sup>c</sup>	-- <sup>d</sup>	-- <sup>c</sup>	-- <sup>c</sup>	87	79	89
Zr	40	82	-- <sup>c</sup>	-- <sup>c</sup>	77	76	-- <sup>c</sup>
BrO <sub>3</sub> <sup>-</sup>	36	7.2	36	69	93	78	91
ClO <sub>3</sub> <sup>-</sup>	29	-- <sup>c</sup>	29	83	94	84	93
IO <sub>3</sub> <sup>-</sup>	27	-- <sup>c</sup>	27	78	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>
NO <sub>2</sub> <sup>-</sup>	68	-- <sup>c</sup>	-- <sup>c</sup>	56	30	83	89
S <sup>2-</sup>	-- <sup>c</sup>	52	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>
SO <sub>3</sub> <sup>2-</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	-- <sup>c</sup>	87	88	-- <sup>c</sup>

<sup>a</sup>Diverse element or ion added at level of 1000-fold ratio of As, Se, Sb, Te, Bi, Sn and Pb (refs 34-36, 41,43); <sup>b</sup>Relative to 100 for emission intensity of As, Se and Sb (0.1 µg/mL), Te, Bi, Sn and Pb (1.0 µg/mL); <sup>c</sup>No interference; <sup>d</sup>Not examined

Table 6. Single-element determination of arsenic, selenium, antimony, tellurium, bismuth, tin and lead in steels by high power N<sub>2</sub>-MIP-AES with hydride generation

Analyte	Sample	Certified value (µg/g)	Present work <sup>a</sup> (µg/g)	Reference
Arsenic	JSS 171-7	460	457 ± 12	34
	JSS 170-7	320	310 ± 13	
	JSS 168-7	120	115 ± 9	
Selenium	NAS8F	2000 <sup>e</sup>	1918 ± 15	34
	NIST 339	2470	2447 ± 27	
Antimony	JSS 172-7	22	20 ± 2	36
	JSS 173-5	50	47 ± 4	
	JSS 174-5	97	94 ± 5	
	JSS 175-7	200	197 ± 11	
Tellurium	JSS 191-1	16	18 ± 3	35
	JSS 192-1	31	26 ± 5	
	JSS 193-1	26	24 ± 2	
	JSS 195-1	42	40 ± 3	
	JSS 190-1	7	N.D. <sup>b</sup>	41
	JSS 191-1	22	N.D.	
Bismuth	JSS 192-1	98	90 ± 13	
	JSS 193-1	34	28 ± 10	
	JSS 195-1	32	27 ± 7	
	NIST 363	80	74 ± 12	
	JSS 168-7	65	60 ± 9	43
Tin	NIST 1765	20	16 ± 7	
	NIST 361	100	92 ± 9	
	NIST 363	19	19 ± 1	44
Lead	BCS 458/1	78	76 ± 4	

<sup>a</sup>The mean ± standard deviation, based on three (for As and Se), five (for Sb, Te, Bi and Sn), and eight (for Pb) replicate determinations; <sup>b</sup>Not determinable; <sup>c</sup>Reference value

Table 7. Analytical figures of merit for the two-element determination of arsenic and antimony, and bismuth and tellurium by high power N<sub>2</sub>-MIP-AES with hydride generation

	Analyte			
	Arsenic	Antimony	Bismuth	Tellurium
Linear dynamic range	10 - 10,000 ng/mL (1 - 1,000 µg/mL) <sup>a</sup>	10 - 10,000 ng/mL (1 - 1,000 µg/mL)	300 - 30,000 ng/mL (10 - 1,000 µg/mL)	300 - 30,000 ng/mL (3 - 1,000 µg/mL)
Detection Limit (3σ)	4.13 ng/mL (650 ng/mL)	4.19 ng/mL (590 ng/mL)	110 ng/mL (4,120 ng/mL)	86 ng/mL (1,570 ng/mL)
Correlation coefficient	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)

<sup>a</sup>Conventional solution nebulizationTable 8. Analytical figures of merit for the three-element determination of arsenic, antimony and bismuth by high power N<sub>2</sub>-MIP-AES with hydride generation

	Analyte		
	As	Sb	Bi
Linear dynamic range	30 - 10,000 ng/mL (1 - 1,000 µg/mL) <sup>a</sup>	30 - 10,000 ng/mL (1 - 1,000 µg/mL)	300 - 10,000 ng/mL (10 - 1,000 µg/mL)
Detection Limit (3σ)	7.13 ng/mL (610 ng/mL)	14.6 ng/mL (580 ng/mL)	116 ng/mL (3,700 ng/mL)
Correlation coefficient	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)

<sup>a</sup>Conventional solution nebulization

preferable to reduce Fe (III) to Fe (II). L-ascorbic acid (34,39,80,81), L-cysteine (57,63,72-74) and thiourea (34,36,77,80,82) as interference-releasing agents have been used for such hydride-forming elements. In contrast with the previously mentioned results, the presence of Fe (III) caused no significant interference for selenium determination, while it was found that the presence of Cr and Ni as minor constituents of steels gave rise to a small suppressing interference. It was found that this interference could be overcome by simply increasing the concentration of sodium tetrahydroborate (III) to 0.6% from the optimized concentration of 0.4%, as already mentioned in Ref. 34. The results found by using the proposed methods are shown in Table 6. The determined concentrations of arsenic, selenium, antimony, tellurium, bismuth, tin and lead in the certified standard samples of steels were in fairly good agreement with the certified values. Consequently, the presented methods were successfully applied to the single-element determination of the above-mentioned elements in steels.

### Multi-element determination by high power N<sub>2</sub>-MIP-AES coupled with hydride generation technique

*Simultaneous determination of two, three and four elements by high power N<sub>2</sub>-MIP-AES coupled with hydride generation technique*

#### *Optimization of experimental conditions and analytical performance*

The simultaneous determination of 2 (arsenic & antimony, and bismuth & tellurium), 3 (arsenic, antimony and bismuth) and 4 elements (arsenic, antimony, bismuth and selenium) by high power N<sub>2</sub>-MIP-AES coupled with hydride generation technique has been investigated. The optimized experimental conditions of the conventional solution nebulization and hydride generation methods used are described in Ref. 37, 39, 40 and 42. Under optimized operating conditions, the linear dynamic ranges and detection limits for these two, three and four element determinations are shown in Tables 7-9, respectively. As a result, with the use of the hydride generation method, the sensitivity for these elements could be found to be greatly improved as compared with a conventional solution nebulization method. For the other methods shown in Table 4, the detection limits of arsenic, antimony, selenium, bismuth and tellurium are lower than those obtained by the present high power N<sub>2</sub>-MIP-AES with hydride

Table 9. Analytical figures of merit for the four-element determination of arsenic, antimony, bismuth and selenium with hydride generation

	Analyte			
	As	Sb	Bi	Se
Linear dynamic range	10 - 30,000 ng/mL (1 - 1,000 µg/mL) <sup>a</sup>	30 - 30,000 ng/mL (1 - 1,000 µg/mL)	300 - 30,000 ng/mL (10 - 1,000 µg/mL)	100 - 30,000 ng/mL (3 - 1,000 µg/mL)
Detection Limit (3σ)	7.80 ng/mL (680 ng/mL)	14.5 ng/mL (910 ng/mL)	131 ng/mL (3,790 ng/mL)	28.99 ng/mL (1,830 ng/mL)
Correlation coefficient	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)	0.999 (0.999)

<sup>a</sup>Conventional solution nebulization

generation technique. However, the proposed method allows a rapid simultaneous determination in a variety of real samples without any separation of matrix.

#### Pre-reduction steps

As previously mentioned, the generation efficiencies of the hydrides from the various oxidation states of arsenic, antimony, selenium and tellurium differ in the hydride generation technique (65-69). As (III) and Sb (III) solutions gave much larger emission intensities than the same concentrations of As (V) and Sb (V), i.e., the ratios of intensities obtained from As (V) and Sb (V) to those from As (III) and Sb (III) for the simultaneous determination of two, three and four elements were approximately 0.26 and 0.27, 0.30 and 0.15, and 0.38 and 0.42, respectively, under the optimized experimental conditions in Refs. 37, 39, 40 and 42. Also, Te (IV) and Se (IV) solution gave much larger emission intensities than the same concentration of Te (VI) and Se (VI), i.e., the ratios of intensities obtained from Te (VI) and Se (VI) to those from Te (IV) and Se (IV) for the simultaneous determination of two and four elements were approximately 0.30 and 0.01%, respectively, under the optimized experimental conditions in Refs. 40 and 42. Therefore, the higher oxidation states of these elements must be reduced to the lower ones prior to hydride generation for the simultaneous multi-element determination of total arsenic, antimony, selenium and tellurium. Of the several reductants investigated, thiourea was found to be the most preferable to pre-reduce arsenic and antimony prior to hydride generation for the simultaneous determination of the two and three elements. Also, after a heating procedure in 5 M hydrochloric acid at 80°C for 20 min, the addition of 50% potassium iodide by the on-line system (a in Figure 1)

was found to be the most preferable method to pre-reduce arsenic, antimony and selenium for the simultaneous determination of the four elements. On the other hand, it is also well known that tellurium is present as Te (IV) in *aqua regia* solution (35,83). In the simultaneous determination of bismuth and tellurium, by using the same concentration solutions of Te (IV) and Te (VI) separately prepared in *aqua regia*, it could be confirmed that the tellurium was present as Te (IV) in *aqua regia* solution. Therefore, the tellurium in steels dissolved in *aqua regia* was determined without the use of such a pre-reduction procedure.

#### Effect of diverse elements

Under the optimized experimental conditions used here, the effects of various other elements on the determination of 2 (arsenic & antimony, and bismuth & tellurium), 3 (arsenic, antimony and bismuth) and 4 elements (arsenic, antimony, bismuth and selenium) by the present hydride generation-high power N<sub>2</sub>-MIP-AES system were examined. The suppressing interferences from some elements are shown in Table 10. As shown in Table 10, a number of elements interfered with the simultaneous determination of arsenic, antimony, bismuth, selenium and tellurium by the present technique. In particular, the presence of Co, Cu, Fe (III), Ni, W and NO<sub>2</sub><sup>-</sup> gave rise to a significant interference when the proposed method was used. In contrast, Pb and Zn did not interfere with single and two element determination of As and Sb. In addition, Cd did not interfere with single or three element determination of As and Sb, as shown in Tables 5 and 10.

Table 10. Effect of diverse elements or ions on the multi-element determination of two (arsenic and antimony, bismuth and tellurium), three (arsenic, antimony and bismuth) and four elements (arsenic, antimony, bismuth and selenium) by high power N<sub>2</sub>-MIP-AES with hydride generation

Element or ion <sup>a</sup>	Relative intensity <sup>b</sup>										
	Bi	Te	As	Sb	As	Sb	Bi	As	Sb	Bi	Se
Al	-- <sup>c</sup>	--	--	67.4	--	--	--	--	--	--	--
Cd	80.3	83.2	--	--	--	--	86.1	58.8	93.0	2.3	2.5
Co	86.7	75.9	34.9	22.2	31.8	19.9	45.9	33.9	30.4	84.4	36.8
Cr(III)	--	--	--	75.4	--	--	--	--	--	--	--
Cr(VI)	88.9	--	25.2	27.6	57.2	30.8	--	86.5	72.1	71.1	43.3
Cu	80.5	81.1	56.3	56.9	68.7	61.5	33.6	45.6	38.5	31.7	3.0
Fe(III)	79.8	73.1	34.5	38.6	34.8	28.4	32.1	27.3	33.7	42.8	24.3
In	--	--	--	--	--	--	--	--	--	--	20.4
Ni	88.4	89.4	14.5	18.9	13.8	18.2	12.9	22.9	24.9	9.2	6.1
Pb	84.8	90.6	--	--	86.7	89.4	--	56.3	83.9	65.7	1.3
Ti	--	83.5	--	--	--	--	--	--	--	--	2
V	81.6	--	25.1	21.5	83.1	83.7	94.8	70.7	85.6	--	77.5
W	75.9	86.7	90.9	30.3	82.8	86.1	94.0	74.5	35.6	18.4	52.5
Zn	88.1	91.3	--	--	84.0	90.4	--	64.4	60.0	--	74.3
BrO <sub>3</sub> <sup>-</sup>	90.8	88.7	24.7	24.8	31.4	18.7	--	29.9	17.3	--	3.2
ClO <sub>3</sub> <sup>-</sup>	92.7	89.1	27.5	26.8	36.9	25.6	--	37.1	36.9	68.2	3.9
IO <sub>3</sub> <sup>-</sup>	--	80.3	29.5	24.4	33.6	36.1	--	25.5	33.3	--	1.7
NO <sub>2</sub> <sup>-</sup>	90.3	82.6	36.4	49.2	33.0	31.1	82.4	61.6	27.3	61.6	0.8

<sup>a</sup>Diverse element or ion added at level of 1000-fold ratio of As, Sb, Bi, Se and Te (refs 37,39,40,42);

<sup>b</sup>Relative to 100 for emission intensity of Bi and Te (1 µg/mL); As and Sb (0.2 µg/mL); As (0.5 µg/mL), Sb (0.5 µg/mL) and Bi (1.0 µg/mL); and As, Sb (1 µg/mL), Bi and Se (5 µg/mL); <sup>c</sup>No interference

#### *Simultaneous determination of two, three and four elements in steels*

In order to demonstrate the effectiveness of the present method for practical analysis, some standard reference materials of steels were analyzed for 2 (arsenic & antimony, and bismuth & tellurium), 3 (arsenic, antimony and bismuth) and 4 elements (arsenic, antimony, bismuth and selenium) using the hydride generation-high power N<sub>2</sub>-MIP-AES. The certified reference materials of steels issued by JSS, NIST and European Committee for Iron and Steel Standardization (EURONORM) were used. As shown in Table 10, it was expected that Fe (III), a major constituent of the steels, was likely to interfere with the simultaneous determination of these

two, three and four elements by the proposed method. In contrast, the presence of Fe (II) showed little or no significant interference. In other words, this means that the Fe (III) in the sample solution must be reduced to Fe (II) by an appropriate reductant and/or interference-releasing agent prior to hydride generation. Of the several interference-releasing agents examined, 1.0% L-ascorbic acid and 0.05 M thiourea for arsenic and antimony, 1.5 and 2.0% L-ascorbic acid for bismuth and tellurium, and for arsenic, antimony and bismuth, respectively, were found to be the most preferable for the reduction of Fe (III) to Fe (II). Also, 0.4% thiourea added by the on-line system (b in Figure 1) as an interference-releasing agent has been used for arsenic, antimony, bismuth and selenium.

Table 11. Two-element determination of bismuth and tellurium in steels by high power N<sub>2</sub>-MIP-AES with hydride generation

Sample <sup>a</sup>	Certified value (μg/g)		Present work (μg/g) <sup>b</sup>	
	Bismuth	Tellurium	Bismuth	Tellurium
JSS 192-1	98	31	93.2 ± 7	35.1 ± 4
JSS 193-1	34	26	39.3 ± 4	28.4 ± 5
JSS 195-1	32	42	35.8 ± 3	45.0 ± 8

<sup>a</sup>Carbon Steels for Minor Elements Determination Series C issued by The Japan Iron and Steel Federation; <sup>b</sup>The mean ± standard deviation, based on five replicate determinations

Table 12. Three-element determination of arsenic, antimony and bismuth in steels by high power N<sub>2</sub>-MIP-AES with hydride generation

Sample	Certified value (μg/g)			Present work (μg/g) <sup>a</sup>		
	Arsenic	Antimony	Bismuth	Arsenic	Antimony	Bismuth
EURONORM 097-1	51	10	5	55 ± 3	7 ± 1	N.D. <sup>b</sup>
NIST 361	170	42	(40) <sup>c</sup>	177 ± 2	36 ± 0.1	N.D.
NIST 363	100	20	(80)	101 ± 2	16 ± 1	70 ± 7

<sup>a</sup>The mean ± standard deviation, based on five replicate determinations; <sup>b</sup> Not determinable;

<sup>c</sup>Reference value

Table 13. Four-element determination of arsenic, antimony, bismuth and selenium in steels by high power N<sub>2</sub>-MIP-AES with hydride generation

Sample	Certified value (μg/g)				Present group (μg/g) <sup>a</sup>			
	Arsenic	Antimony	Bismuth	Selenium	Arsenic	Antimony	Bismuth	Selenium
NIST 361	170	42	(40) <sup>c</sup>	40	179 ± 8 (179 ± 13) <sup>d</sup>	39 ± 6 (42 ± 3)	N.D. <sup>b</sup> N.D.	37 ± 5 (34 ± 4)
NIST 363	100	20	(80)	16	94 ± 2 (89 ± 9)	19 ± 1 (19 ± 9)	73 ± 8 (73 ± 9)	19 ± 3 (16 ± 8)

<sup>a</sup>The mean ± standard deviation, based on five replicate determinations; <sup>b</sup> Not determinable; <sup>c</sup>Reference value;

<sup>d</sup>Obtained by using thiourea as a releasing agent

The results by the proposed methods are shown in Tables 11-13. The result of the simultaneous determination of arsenic and antimony was reported in Ref. 37. The determined concentrations of arsenic, antimony, selenium, bismuth and tellurium in the certified materials of steels were in good agreement with the certified values. The presented methods were successfully applied to the multi-element determination of steels.

## Conclusions

The characteristics of a recently introduced annular-shaped high power N<sub>2</sub>-MIP have been described in this review, and it has been demonstrated that such an

uncommon plasma spectrochemical source can be successfully used for the single-element determination of trace concentrations of some hydride-forming elements, i.e., arsenic, antimony, bismuth, selenium, tellurium, tin and lead in steels. The detection limits of this hydride generation-high power N<sub>2</sub>-MIP-AES system for these hydride-forming elements are greatly improved compared with conventional solution nebulization. This dramatic improvement in detection limit could make the determination of trace amounts of these elements by hydride generation-high power N<sub>2</sub>-MIP-AES practical for a wide range of samples. Also, the simultaneous determination for 2 (arsenic & antimony, and bismuth & tellurium), 3 (arsenic, antimony and bismuth) and 4

elements (arsenic, antimony, bismuth and selenium) by the proposed techniques was successfully applied to the determination of low concentrations of these elements in steels. It should be stressed that the proposed technique offers a rapid determination procedure without any separation of the iron matrix. The application of this technique appears to be promising and its extension to other hydride forming elements is currently underway in this laboratory.

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