High Power Nitrogen Microwave Induced Plasma for the Determination of Some Trace Elements in Steels by Atomic Emission Spectrometry with Hydride Generation Technique

Taketoshi NAKAHARA

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

An annular-shaped high power nitrogen microwave induced plasma (N₂-MIP) sustained at atmospheric pressure by an Okamato cavity has been used as a new excitation source for atomic emission spectrometry (AES). In the preliminary study of high power N₂-MIP-AES, the background equivalent concentrations and detection limits for a number of elements were measured at the most sensitive wavelengths of the elements by using a conventional solution nebulization as a sample introduction method. The detection limits obtained for the elements of interest are inferior by approximately one to two orders of magnitude compared with those obtained in this laboratory by a conventional argon inductively coupled plasma atomic emission spectrometry with solution nebulization. Subsequently, the combination of high power N₂-MIP-AES with continuous-flow hydride generation technique was examined for the sensitive determination of such hydride-forming elements as antimony, arsenic, selenium and tellurium. Under the optimized experimental conditions, the best attainable detection limits at Sb(I)217.581, As(I)228.812, Se(I)196.026 and Te(I)214.281 nm by use of N₂-MIP-AES coupled with hydride generation were 4.46 ngSb/ml, 2.99 ngAs/ml, 0.86 ngSe/ml and 15.0 ngTe/ml with linear dynamic ranges of three to four orders of magnitude in concentrations. After the interference study, the present method has been applied to the determination of trace concentrations of the above-mentioned hydride-forming elements in several steel standard reference materials issued by The Japan Iron and Steel Federation. The results obtained by the proposed method were in good agreement with the certified values.

KEY WORDS: high power nitrogen microwave induced plasma; Okamato cavity; atomic emission spectrometry; hydride generation method; antimony; arsenic; selenium; tellurium; steels.

1. Introduction

Many kinds of plasma sources have been widely investigated and used for trace element analysis by atomic emission spectrometry (AES) or mass spectrometry (MS). At present, the most popular plasma source is an argon inductively coupled plasma (Ar-ICP). In general, both Ar-ICP-AES and Ar-ICP-MS have enjoyed widespread use in a variety of practical samples, because they can give high sensitivity and good precision in trace elemental analysis. However, for instance, 39K+, 40Ca+, 52Cr+, 56Fe+ and 80Se+ cannot be determined directly by Ar-ICP-MS, because the determination of these elements suffers from severe interferences of 39ArH+, 40Ar+, 44ArC+, 44ArO+ and 44Ar²+, respectively, that are caused by the plasma sustained gas (i.e., Ar) of the Ar-ICP. Therefore, other types of plasma sources such as microwave induced plasmas (MIPs) have been explored and examined by a number of researchers. Existing microwave plasma systems, including Beenakker cavity, the surfatron and the microwave plasma torch (MPT) are subject to a number of serious limitations. Usually, the input microwave power of these MIPs is operated at 200-300 W (up to 500 W), and therefore they cannot provide sufficient plasma energy to desolvate, atomize, excite and ionize many elements from a directly nebulized sample solution. More recently, the kilowatt-plus helium microwave induced plasma system (KiP-MIP) was developed and investigated by Carnahan's group. Because the KiP-MIP is of high power (1600 W), the expected analytical performance is more effective than that of low powered MIPs. However, such a MIP as one produced by either the Beenakker cavity or the surfatron, is subject to a number of serious limitations. In addition to, most importantly, its low tolerance to liquid aerosol, it was impossible to produce an annular-shaped (toroidal) plasma similar to an Ar-ICP. In order to overcome these limitations, recently, Okamato has developed and described a new cavity-torch arrangement being able to produce an annular-shaped high power (up to 1.5 kW) nitrogen MIP at atmospheric pressure, originally for mass spectrometry (MS), the total system of which has been commercially available in the market. This high power nitrogen microwave-induced plasma (N₂-MIP) is mentioned to tolerate the continuous, direct introduction (i.e., without need for desolvation) of wet aerosols produced with a nebulizer-spray chamber assembly as used in ICP-AES.
Furthermore, the N₂-MIP doesn’t become unstable and is not extinguished even if an air sample is injected and also a hydride generation technique to be mentioned below is combined in the continuous mode. Surprisingly, however, only some emission characteristics of this high power N₂-MIP for AES have been investigated to date. Very recently Ohata and Furuta and Ogura et al. described the spatial characterization of emission intensities and/or temperatures of a high power N₂-MIP generated by use of an Okamoto cavity. Furthermore, to the best of my knowledge, at present only a few papers have focused on the application of the high power N₂-MIP-AES to the analysis of real-world samples.

In this review, several analytical performances of the high power N₂-MIP-AES will be first described in brief. Subsequently, some results of our recent works on the determination of some hydride-forming elements (i.e., antimony, arsenic, selenium and tellurium) in combination with both conventional solution nebulization and hydride generation technique are to be mentioned below. The results obtained by both sample introduction methods are compared in terms of analytical figures of merit for these elements. Finally, after the interference study for each element, the present method coupled with hydride generation technique has been successfully applied to the determination of concentrations of antimony, arsenic, selenium and tellurium in samples of several standard reference materials of steels. The detailed fundamentals and applications of the hydride generation techniques for analytical atomic spectrometry, e.g., ICP-AES, MIP-AES and ICP-MS can be found from some survey articles prepared by the present author and then are not mentioned at all in this review.

2. Experimental

2.1. Instrumentation and Apparatus

A schematic diagram of the experimental apparatus for hydride generation-high power N₂-MIP-AES is shown in Fig. 1. An Okamoto cavity was used for the production of the high power N₂-MIP and is shown in Fig. 2. A high power N₂-MIP source together with a magnetron was used in this work are listed in Table 1. An annular-shaped (toroidal) plasma is formed above the quartz torch. The major instruments used in this work are listed in Table 1.

The sample introduction systems included a conventional pneumatic nebulization of solutions and a hydride generation technique. For hydride generation, a drying flask (Fig. 1) filled with concentrated sulfuric acid was installed between a gas-liquid separator and a nebulizer chamber to remove the water vapor produced during hydride generation.

Table 1. Experimental instrumentation for high power N₂-MIP-AES

| Component          | Model                      | Manufacturer       |
|--------------------|----------------------------|--------------------|
| Microwave generator| MKN-103-3S                 | Nippon Kousyuha    |
| Microwave cavity   | Okamoto cavity             | Hitachi            |
| MIP torch          | 300-8352                   | Hitachi            |
| Spectrometer       | Part of ICAP-575           | Nippon Jarrell-Ash |
| Photomultipliers   | R427 & R550                | Hamamatsu Photonics |
| Personal computer  | PC-9801EX                  | NEC                |
| Peristaltic pump   | MP-3                       | Tokyo Rikakikai    |
3.1. General Analytical Performance of High Power N₂-MIP-AES

In the preliminary study of high power N₂-MIP-AES, detection limits of a number of elements as some of analytical figures of merit were measured by a conventional solution nebulization and the background equivalent concentration (BEC) and detection limit (DL) obtained for a number of elements are given in Table 3. Detection limits (DLs) for the elements were extrapolated from the linear calibration graphs and were defined as the concentration of the analyte that would produce a net signal (i.e., background-corrected line intensity, Iₐ) equal to three times the standard deviation of the background emission intensity (Iₑ), in accordance with IUPAC recommendation.⁵⁴

Table 3. Detection limits for various elements by high power N₂-MIP-AES with conventional solution nebulization

| Element  | Energy level (eV) | BEC* (μg/ml) | DLb (ng/ml) |
|----------|------------------|--------------|-------------|
| Ag (I)   | 338.29           | 3.66 - 0.0   | 0.18        | 1.49        |
| Al (I)   | 394.40           | 3.14 - 0.0   | 0.38        | 36.3        |
| As (I)   | 228.81           | 6.77 - 1.35  | 89.5        | 3690.4      |
| Au (I)   | 267.60           | 4.63 - 0.0   | 0.79        | 24.8        |
| B (I)    | 249.77           | 4.96 - 0.0   | 2.42        | 98.1        |
| Ba (II)  | 455.40           | 2.72 - 0.0   | 0.006       | 1.38        |
| Be (II)  | 331.10           | 3.96 - 0.0   | 0.36        | 3.85        |
| Bi (I)   | 306.77           | 4.04 - 0.0   | 10.5        | 209.6       |
| Ca (II)  | 593.37           | 3.15 - 0.0   | 0.016       | 1.01        |
| Cd (II)  | 228.80           | 5.42 - 0.0   | 2.31        | 71.8        |
| Co (II)  | 345.35           | 4.02 - 0.43  | 1.10        | 92.8        |
| Cr (III) | 425.43           | 2.91 - 0.0   | 0.12        | 8.85        |
| Cu (I)   | 324.75           | 3.82 - 0.0   | 0.068       | 7.13        |
| Fe (I)   | 371.99           | 3.33 - 0.0   | 0.58        | 13.7        |
| Ga (I)   | 417.21           | 3.07 - 0.10  | 1.59        | 60.1        |
| Ge (I)   | 303.91           | 4.96 - 0.88  | 2.58        | 153.4       |
| Hg (I)   | 253.65           | 4.89 - 0.0   | 8.39        | 250.9       |
| In (I)   | 451.13           | 3.02 - 0.27  | 1.02        | 90.3        |
| K (I)    | 766.49           | 1.62 - 0.0   | 3.54        | 1075.0      |
| Mg (I)   | 285.21           | 4.35 - 0.0   | 0.11        | 2.17        |
| Mn (I)   | 279.48           | 4.43 - 0.0   | 0.66        | 1.0         |
| Na (I)   | 589.00           | 2.10 - 0.0   | 0.20        | 26.7        |
| Ni (I)   | 341.48           | 3.66 - 0.03  | 0.28        | 14.1        |
| P (I)    | 253.57           | 7.21 - 2.32  | 193.9       | 6818.3      |
| Pb (I)   | 405.78           | 4.38 - 1.32  | 1.64        | 87.5        |
| Sb (I)   | 217.58           | 5.70 - 0.0   | 16.8        | 875.3       |
| Se (I)   | 196.03           | 6.32 - 0.0   | 156.0       | 4789.4      |
| Sn (II)  | 326.23           | 4.87 - 1.07  | 4.0         | 25.4        |
| Sr (II)  | 407.77           | 3.04 - 0.0   | 0.008       | 0.95        |
| Te (I)   | 214.28           | 5.78 - 0.0   | 54.6        | 1349.7      |
| Ti (I)   | 377.57           | 3.28 - 0.0   | 3.64        | 126.3       |
| V (II)   | 310.23           | 4.36 - 0.37  | 0.78        | 22.6        |
| Zn (I)   | 213.86           | 5.80 - 0.0   | 6.12        | 124.3       |

a. Background equivalent concentration.
b. Detection limit.

It can be concluded here from the results shown in Table 3 that the DLs for the elements of interest obtained by high power N₂-MIP-AES are inferior by approximately one to two orders of magnitude compared with those obtained in this laboratory by a conventional Ar ICP-AES with solution nebulization in part owing to its diatomic molecules, including possible quenching of excited analyte species.⁵⁹

In addition, some typical emission spectra of arsenic obtained by hydride generation high power N₂-MIP-AES are shown in Fig. 3, in which relatively small background emission spectra around the arsenic emission lines are noticed to a great extent.

3.2. Determination of Antimony by High Power N₂-MIP-AES

Some of the optimum operating conditions given in Table 2 will be discussed below.

3. Results and Discussion
3.2.1. Optimization of Experimental Conditions

The background-corrected line intensities (Ib), line-to-background intensity ratios (I/Ib) and background equivalent concentrations (BEC) were measured at the major emission lines (206.833, 217.581, 231.147 and 259.805/259.809 nm) of antimony after hydride generation or conventional solution nebulization. The Sb(I) 259.805/259.809-nm doublet could not be separated by the spectrometer used. In addition, the Sb(II) 252.852 nm line suffers from a strong coincident interference of the Si(I) 252.851-nm line in the case of the hydride generation high power N2-MIP-AES as a result of the significant abrasion of the quartz tube by the discharge so that this antimony line cannot be used for analysis. As a result, the 231.147-nm line was throughout used as the analytical line, except where noted.

![Typical MIP emission spectra in the wavelength ranges of 187-202, 227-237 and 273-288 nm with continuous-flow hydride generation of a 2.0 μg/ml arsenic solution.](image)

**Fig. 3** Typical MIP emission spectra in the wavelength ranges of 187-202, 227-237 and 273-288 nm with continuous-flow hydride generation of a 2.0 μg/ml arsenic solution.

3.2.2. Pre-Reduction Step

Hydride generation in atomic spectroscopy including plasma emission spectrometry is often dependent on the oxidation state of the analyte elements such as antimony, and the present hydride generation-N2-MIP-AES was expected to exhibit such an effect. In the absence of a pre-reductant, antimony(III) gave a higher sensitivity than antimony(V) and a Sb(V) : Sb(III) intensity ratio of 0.31 was found under the experimental conditions given in Table 2. Therefore, antimony(III) must be reduced to antimony(II) prior to hydride generation for the determination of total antimony (i.e., Sb(III) + Sb(V)).

Pre-reduction of antimony(V) to antimony(III) has been achieved by the addition of a number of reagents. In the present work, the use of potassium iodide, thiourea and L-cysteine was evaluated in the acidity of 1.0 M hydrochloric acid. As a consequence, L-cysteine, the use of which had been previously described in the literature on hydride generation atomic absorption spectrometry (AAS), was found to be the most effective in the pre-reduction of Sb(V) to Sb(III) in this work. The results of the use of L-cysteine show that the addition of more than 0.1 % L-cysteine is effective for the pre-reduction and so in the following study, 2 % L-cysteine was added as a pre-reductant for the determination of total antimony. As will be described below, L-cysteine serves as not only a pre-reductant, but also an effective masking agent in eliminating or minimizing some depressing interferences from diverse elements including iron as a major constituent of steels.

3.2.3. Analytical Working Curves, Detection Limits and Precisions

Under the optimized operating conditions depicted in Table 2, double logarithmic analytical working graphs were obtained for arsenic at 231.147 nm with use of freshly prepared antimony(III) solutions by both a conventional solution nebulization and a hydride generation technique. Some analytical figures of merit for antimony obtained from the analytical working graphs (not shown here) are as follows. The DL, the definition of which has been already mentioned, at Sb(I) 231.147 nm by high power N2-MIP-AES coupled with hydride generation was 1.87 ng/ml with a linear dynamic range of 50 to 5000 ng/ml, while the DL obtained by use of conventional solution nebulization was 0.51 μg/ml with a linear dynamic range of 1 to 1000 μg/ml. In particular, the DL obtained by the present hydride generation high power N2-MIP-AES are fairly poorer than the DLs obtained by either Ar-ICP-AES (DLs within 0.1 and 2 ng/ml, typically around 0.5-1 ng/ml) or He-MIP-AES (a typical DL of 0.5 ng/ml) coupled with hydride generation.

3.2.4. Effect of Diverse Elements

It has been reported in the literature that the determination of antimony by hydride generation atomic spectrometry is susceptible to interferences from various diverse elements. Under the experimental conditions used here, the effect of various other elements on the antimony determination by the present hydride generation-high power N2-MIP-AES was examined. Interference is considered to have occurred when an emission intensity is changed by over ±5% from that for antimony alone. The following elements or ions at levels a 1000-fold greater than antimony interfered: Ag, As, Au, Bi, Co, Cd, Cr(VI), Cu, Fe(III), Ni, Pd, Se, Te, W, BrO3-, ClO3- and IO3-.

The usefulness of L-cysteine for reduction of antimony(V) to antimony(III) prior to stibine generation was already described above. In order to minimize or eliminate depressing interferences from diverse elements in hydride generation-atomic spectrometry, many workers have added several different kinds of masking agents and used some separation procedures. In the present hydride generation high power N2-MIP-AES of antimony, potassium iodide, thiourea, 1,10-phenanthroline, L-cysteine and EDTA were investigated as potential masking agents and added to the acidified sample solution. As a result, L-cysteine, the use of which had been previously described in the literature on hydride generation-AAS, was again
found to be the most effective of the masking additives examined. L-cysteine (2%) can serve as an effective masking agent in eliminating or minimizing some depressing interferences from diverse elements including iron as a major constituent of steel samples.

3.2.5. Application to the Determination of Antimony in Steels

On the basis of the observations described above, the present hydride generation high power N$_2$-MIP-AES was applied to the determination of low concentrations of antimony in the standard reference materials of steels

Sample digestion procedure is as follows. A 0.5-g steel sample was dissolved in 10 ml of aqua regia (3:1 by volume of HCl and HNO$_3$) by heating slowly on a hot plate. After complete dissolution, approximately 50 ml of Milli-Q water and 20 ml of 20% L-cysteine was added and the sample solution was further diluted exactly to 100 ml with hydrochloric acid and Milli-Q water to give a final acidity of 1.0 M hydrochloric acid.

It was expected that iron as the matrix constituent of the samples, at greater than 1000-fold weight ratio to antimony was likely to interfere with the determination of antimony by the proposed method even in the presence of 2% L-cysteine. A recovery study was carried out by adding known amounts of antimony(III) to the acidified sample solutions together with a concentration (2%) of L-cysteine and applying the operating conditions given in Table 2. The recovery of the added antimony was almost quantitative (98 ± 2.5%, n = 5), so that a calibration graph method could be employed in the antimony determination. Antimony was determined in four samples of carbon steels and the results calculated by least-squares analysis are presented in Table 4. The determined concentrations of antimony in the samples are in good agreement with the reference values.

Table 4. Determination of antimony in steel samples by hydride generation high power N$_2$-MIP-AES

| Sample*   | Antimony content (µg/g) |
|-----------|-------------------------|
|           | Certified value | Present work* |
| JSS 172-7 | 22              | 20 ± 1 (n = 5) |
| JSS 173-5 | 50              | 47 ± 2 (n = 5) |
| JSS 174-5 | 97              | 94 ± 5 (n = 5) |
| JSS 175-7 | 200             | 197 ± 11 (n = 5) |

a. "Carbon Steel for Minor Elements Determination Series B" issued by The Japan Iron and Steel Federation.
b. The mean ± standard deviation (number of determinations).

3.3 Determination of Arsenic and Selenium by High Power N$_2$-MIP-AES

3.3.1. Optimized Experimental Conditions

In the preliminary study, major emission lines for arsenic (188.979, 193.696, 197.262, 200.334 and 228.812 nm) and selenium (196.026, 199.511, 203.985, 206.279 and 207.479 nm) were observed in the spectral range of 185 to 290 nm. Some typical emission spectra for arsenic obtained by hydride generation high power N$_2$-MIP-AES have been depicted already in Fig. 3. As a consequence, the As(I) 228.812- and Se(I) 196.026-nm lines were selected and used for the arsenic and selenium determinations, respectively, throughout in the following study.

3.3.2. Detection Limits for Arsenic and Selenium

Under the optimized operating conditions, double logarithmic analytical working graphs were obtained for arsenic and selenium at 228.812 and 196.026 nm, respectively, with use of freshly prepared arsenic(III) and selenium(IV) solutions by both a conventional solution nebulization and a hydride generation technique. The best attainable detection limits by use of high power N$_2$-MIP-AES coupled with hydride generation technique were 2.99 ngAs/ml and 0.86 ngSe/ml with linear dynamic ranges of 5 to 10000 ngAs/ml and 1 to 5000 ngSe/ml. These detection limits obtained by the present hydride generation high power N$_2$-MIP-AES are somewhat poorer than those obtained by ICP-AES coupled with hydride generation.

3.3.3. Pre-Reduction Procedure

It is well known that the arsenic and selenium may be present in practical samples in two typical oxidation states, +3/+5 and +4/+6, respectively, which exhibits pronounced differences in their hydride generation efficiency. Most determinations of the total arsenic and selenium, therefore, call for a pre-reduction step of arsenate(As$_5^+$) and selenate(Se$_6^-$) to arsenite(As$_3^+$) and selenite(Se$_4^-$), respectively, prior to hydride generation. In this work, the effects of various concentrations of many pre-reductants including potassium iodide, thiourea and L-cysteine in the determination of arsenic and selenium. As a result, the most preferable pre-reductant was potassium iodide of 1.0% (w/v) for the determination of total arsenic in the samples. Furthermore, to pre-reduce Se(VI) to Se(IV) the best way was found to be by heating the selenium solution in the presence of 5.0 M hydrochloric acid at 80°C for 20 min for the determination of total selenium.

3.3.4. Effect of Diverse Elements

The determination of arsenic and selenium by hydride generation-atomic spectrometry is well known to be susceptible to interferences from various diverse elements. Under the experimental conditions used here, the effect of various other elements on the arsenic and selenium determinations was examined. The following elements or ions at concentrations 1000-fold greater than arsenic or selenium interfered: Ag, Au, Co, Cu, Fe(III), Ga, Ge, Ni, Pd, Sb, Se, Te, Ti, Zr, BrO$_3^-$, ClO$_3^-$, IO$_3^-$ and NO$_2^-$ in the determination of arsenic and Ag, As, Au, Bi, Cd, Co, Cr(III), Cu, Ge, In, Ni, Pb, Pd, Sb, Sn, Ti, Zr, BrO$_3^-$ and S$_2^-$ in the determination of selenium.

3.3.5. Application to the Determination of Arsenic and Selenium in Steels

In an attempt to demonstrate that this proposed method is effective for practical analysis, several standard reference materials of carbon steels and stainless steels were analyzed for arsenic and selenium, respectively, using the hydride generation high power N$_2$-MIP-AES.
For carbon steels, sample digestion procedure is as follows. A 0.5-g carbon steel sample was dissolved in 10 ml of *aqua regia* by heating slowly on a hot plate. After complete dissolution, the resultant solution was further diluted exactly to 20 ml with Milli-Q water and then used as a sample solution for the determination of arsenic. For stainless steels, a 0.5-g carbon steel sample was dissolved in 5 ml of *aqua regia* (3:1 by volume of HCl and HNO₃) by heating slowly on a hot plate. After complete dissolution, the resultant solution was further diluted exactly to 20 ml with Milli-Q water and then utilized as a sample solution for the determination of selenium.

It was expected that iron as the matrix constituent of the samples, at greater than 1000-fold weight ratio to arsenic and selenium was likely to interfere with the determination of arsenic and selenium by the proposed method. For the arsenic determination as already mentioned, the presence of iron(III) caused a depressing interference, whereas the presence of iron(II) had little or no significant interference. Therefore, in this case, the iron(III) in the sample solution was pre-reduced to the interference-free iron(II) by addition of ascorbic acid (0.1%). In the determination of arsenic, to the sample solution (20 ml), 10 ml of 20% potassium iodide, 10 ml of 1% ascorbic acid and 6 M hydrochloric acid to give their final concentrations of 2%, 0.1% and 1.0 M, respectively, prior to the final dilution to 100 ml with Milli-Q water. A calibration graph method was employed in the arsenic determination. Arsenic was determined in three samples of carbon steels and the results calculated by least-squares analysis are presented in Table 5. The determined concentrations of arsenic in the samples are in good agreement with the reference values.

### Table 5. Determination of arsenic in steel samples by hydride generation high power N₂-MIP-AES

| Sample* | Arsenic content (µg/g) |
|---------|-----------------------|
|         | Certified value       | Present work* |
| JSS 171-7 | 460                   | 457 ± 12 (n = 3) |
| JSS 170-7 | 320                   | 310 ± 13 (n = 3) |
| JSS 168-7 | 120                   | 115 ± 9 (n = 5)  |

a. "Carbon Steel for Minor Elements Determination Series B" issued by The Japan Iron and Steel Federation.

b. The mean ± standard deviation (number of determinations).

To the contrary as previously mentioned, the presence of iron(III) caused no significant interference with the selenium determination, while it was found that the presence of chromium and nickel as alloying elements of stainless steels gave rise to a small depressing interference. It was found that this interference could be overcome apparently by simply increasing the concentration of sodium tetrahydroborate(III) to 0.6% from the optimized concentration of 0.4% (Table 8). In the determination of selenium, to a 5.0-ml portion of the sample solution, hydrochloric acid was added to give a final concentration of 5.0 M and diluted to 50 ml. The resultant solution was heated on a hot plate at 80°C for 20 min. A recovery study was carried out by adding known amounts of selenium to the acidified sample solutions. The added selenium was recovered in the range 98-104%, depending on the samples. Therefore, a calibration graph method could be employed in the selenium determination. The results for two samples of stainless steel were calculated by least-squares analysis and are shown in Table 6. The results given in Table 9 show good precision and are in good agreement with the certified values.

### Table 6. Determination of selenium in stainless steels by hydride generation high power N₂-MIP-AES

| Sample* | Selenium content (µg/g) |
|---------|-------------------------|
|         | Certified value Present work* |
| Austenitic NAS8F | 2000 | 1918 ± 15 (n = 3) |
| NIST SRM 339 | 2470 | 2447 ± 27 (n = 3) |

a. The mean ± standard deviation (number of determinations).

### 3.4. Determination of Tellurium by High Power N₂-MIP-AES

#### 3.4.1. Optimization of Experimental Conditions

For the major emission lines of tellurium, the background-corrected emission intensities (Iₛ), line-to-background intensity ratios (Iₛ/Iₖ) and background equivalent concentrations (BEC) were measured at 200.202, 214.281, 214.725, 225.902 and 238.578 nm. As a result, the Te(I) 214.281-nm line was selected as an analytical wavelength. The other experimental parameters were investigated in detail and optimized for conventional solution nebulization and hydride generation.

#### 3.4.2. Analytical Figures of Merit

Under the optimized operating conditions, double logarithmic analytical working graphs were obtained for tellurium at 214.281 nm with the use of freshly prepared Te(IV) solutions by both conventional solution nebulization and hydride generation techniques. Detection limits for tellurium were extrapolated from the linear calibration graphs. The detection limit at Te(I) 214.281 nm by high power N₂-MIP-AES coupled with hydride generation was 15.0 ng/ml with a linear dynamic range of 50-5000 ng/ml, while the detection limit obtained by use of conventional solution nebulization was 740 ng/ml with a linear dynamic range of 0.5-500 µg/l. With hydride generation method the sensitivity for tellurium could be found good. The detection limit for As, Se, and Sb was obtained 1.87, 2.99 and 0.86 ng/ml, respectively, by the same hydride generation method. The detection limits for tellurium were reported to be 0.027 ng/ml, 0.3 ng/ml and 0.2 ng/g, respectively.

#### 3.4.3. Pre-Reduction Step

In general, tellurium is present in both the oxidation state of Te(IV) and Te(VI) under acidic solution. The generation efficiencies of tellurium hydride from Te(IV) and Te(VI)
are quite different. In this study, the tellurium(IV) solution gave a larger emission intensity than the same concentration of tellurium(VI), i.e., a ratio of intensity obtained from Te(VI) to that from Te(IV) being approximately 0.3. Therefore, tellurium(VI) in the sample solution must be reduced to Te(IV) prior to hydride generation for the determination of total tellurium [i.e., Te(IV) + Te(VI)].

The most frequently used for pre-reduction of Te(VI) to Te(IV) is to heat the sample with HCl. In this work, the use of potassium iodide, thiourea, L-cysteine, ascorbic acid and hydrochloric acid was evaluated. As a consequence, hydrochloric acid was found to be the most effective in pre-reduction of Te(VI) to Te(IV) in this work. The results of the use of hydrochloric acid are shown in Fig. 7 and show that the heating of the tellurium solution in more than 6 M hydrochloric acid at 80°C for 30 min is very effective in the pre-reduction of Te(VI) to Te(IV).

On the other hand, it is also well known that tellurium exists as Te(IV) in the aqua regia solution. In this work, by using the same concentration solutions of Te(IV) and Te(VI) separately prepared in aqua regia, it could be confirmed that the tellurium is present as Te(IV) in the aqua regia solution. Therefore, tellurium in carbon steels was determined without the use of the above-mentioned pre-reduction procedure.

3.4.4. Determination of Tellurium in Carbon Steels

After an interference study, in order to demonstrate that this system is effective for practical analysis, some standard reference materials of Carbon Steel for Minor Elements Determination Series C issued by The Japan Iron and Steels Federation were analyzed for tellurium using the present hydride generation high power N$_2$-MIP-AES. It was expected that the iron(III) as the matrix constituent of the samples, present at greater than a 100-fold mass ratio to tellurium, was likely to interfere with the determination of tellurium by the proposed method. However, as already mentioned, the presence of Fe(II) showed little or no significant interference. In other words, this means that the iron(III) in the sample solution must be reduced to the iron(II) by an appropriate reductant and/or interference-releasing agent prior to hydride generation. Of the several pre-reductants and/or interference-releasing agents examined, such as thiourea, L-cysteine, ascorbic acid, the addition of 2.0 % (w/v) L-cysteine was found to be the most preferable in the pre-reduction of Fe(III) to Fe(II), but it could give rise to a non-quantitative recovery (i.e., an averaged value of approximately 86 %) for the sample solutions spiked with several known amounts of tellurium. Therefore, a standard additions method was employed in the determination of tellurium in carbon steels as follows.

Approximately 0.5 g sample of carbon steels was weighed accurately and transferred to a 50-ml beaker. Ten ml of aqua regia (3:1 by volume of HCl and HNO$_3$) was added, and the sample was dissolved completely by heating on a hot plate. After cooling at room temperature, the resultant solution was transferred into a 100-ml volumetric flask and diluted to the mark with Milli-Q water. A 20-ml portion of the sample solution was transferred into a 100-ml volumetric flask. After suitable various volumes of Te(IV) standard solution and HCl were added and diluted to the mark with Milli-Q water to give the final solutions containing 0, 0.1, 0.2 and 0.5 mg Te/l and 2 M in HCl. These solutions were utilized for the determination of tellurium using the proposed hydride generation high power N$_2$-MIP-AES. The results obtained are presented in Table 7. The determined concentrations of tellurium in the carbon steel samples are in good agreement with their certified values.

Table 7. Determination of tellurium in steel certified reference materials by continuous hydride generation high power N$_2$-MIP-AES

| Sample* | Tellurium content (µg/g) | Certified value | Present work$^a$ |
|---------|--------------------------|----------------|-----------------|
| JSS 190-1 | 10.0 | 8.0 ± 2 (n=5) |
| JSS 191-1 | 16.0 | 18.0 ± 3 (n=5) |
| JSS 192-1 | 31.0 | 26.0 ± 5 (n=5) |
| JSS 193-1 | 26.0 | 24.0 ± 2 (n=5) |
| JSS 195-1 | 42.0 | 40.0 ± 3 (n=5) |

$^a$"Carbon Steel for Minor Elements Determination Series C" issued by The Japan Iron and Steel Federation.

4. Conclusions

In this review, it has been demonstrated that the present technique using such a not so common plasma spectrochemical source as a high power N$_2$-MIP can be successfully used for the determination of trace concentrations of some hydride-forming elements, i.e., antimony, arsenic, selenium and tellurium in the steel samples. The detection limits for these elements by this hydride generation-high power N$_2$-MIP-AES system are greatly improved over the conventional solution nebulization technique. This dramatic improvement in detection limits could make the determination of traces of the four elements by hydride generation-high power N$_2$-MIP-AES practical for a wide range of samples.

For the determination of the total amounts (i.e., Sb (III+V), As (III+V), Se (IV+VI) and Te (IV+VI)) of antimony, arsenic, selenium and tellurium in the sample, however, the pre-reduction procedure must be carried out in order to convert the analyte's higher oxidation state to the lower one prior to hydride generation. Furthermore, the addition of L-cysteine, potassium iodide or ascorbic acid is in some cases effective in eliminating or minimizing serious interferences from several diverse elements in the determination of these four elements. The use of purer reagents such as sodium tetrahydroborate(III) should make it possible to decrease the background emission including the reagent blank, resulting in some more improvement in the lowest determinable concentration of these four elements as well as in the linear calibration ranges. The application of this technique looks promising and its extension to other hydride-forming...
elements is currently under way in this laboratory.

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