Anal Bioanal Chem (2004) 379 : 90–95
DOI 10.1007/s00216-003-2476-y

SPECIAL ISSUE PAPER

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Simultaneous determination of bismuth and tellurium in steels by high power nitrogen microwave induced plasma atomic emission spectrometry coupled with the hydride generation technique

Received: 21 September 2003 / Revised: 2 December 2003 / Accepted: 11 December 2003 / Published online: 28 January 2004

Abstract An annular-shaped, high power nitrogen microwave induced plasma (N_2-MIP) produced at atmospheric pressure by an Okamoto cavity, as a new excitation source for atomic emission spectrometry (AES), has been used for the simultaneous determination of bismuth and tellurium in steels with the hydride generation method. Under the optimized experimental conditions, the best attainable detection limits at the Bi I 195.389 nm and Te I 200.200 nm lines were 110 and 86 ng/ml for bismuth and tellurium, respectively. The linear dynamic ranges for bismuth and tellurium were 300 to 30,000 ng/ml. The presence of several diverse elements was found to cause a more or less depressing interference with the proposed technique. When bismuth and tellurium in steels were determined, a large amount of Fe(III) in the solution caused a severe depressing interference, while the presence of Fe(II) showed little or no significant interference. Of the several interference-releasing agents examined, L-ascorbic acid was found to be the most preferable to reduce Fe(III) to Fe(II) prior to hydride generation. The concentrations of bismuth and tellurium in steels were determined by the proposed technique. The results obtained by this method were in good agreement with their certified values.

Keywords High power nitrogen microwave induced plasma · Atomic emission spectrometry · Hydride generation technique · Bismuth · Tellurium · L-ascorbic acid · Steels

Introduction

Many types of plasmas have been developed as excitation sources for elemental analysis over many years. One of the most important sources is an argon (Ar) inductively coupled plasma (ICP). Nevertheless, the Ar-ICP has several limitations. For example, polyatomic ions related to plasma sustained in Ar gas interfere with the analytes in mass spectrometry (MS). Also, though the investment cost of ICP spectrometers has been significantly reduced, the operating costs are large because of a large consumption of plasma gas (i.e., argon) in order to sustain the ICP, which has a high excitation temperature and electron density. On the other hand, it is well known that the microwave induced plasma (MIP) has received considerable attention as an alternative powerful excitation source. This source has the advantages of low cost, low gas consumption, and ease of use over an ICP [1]. However, an MIP such as the one produced by either a Beenakker cavity [2, 3], a Surfatron [4, 5] or a microwave torch [6] has some serious limitations, for example, a low power (up to 500 W) and its low tolerance to liquid aerosols.

In order to overcome these limitations, Okamoto [7, 8] has developed a new cavity-torch arrangement that is able to produce a doughnut-shaped, high power (1.0 kW) nitrogen microwave induced plasma (N_2-MIP) at atmospheric pressure, just the same as an Ar-ICP. The Okamoto cavity was originally developed to produce an alternative analytical ionization source to the Ar-ICP for MS. This N_2-MIP can tolerate the direct and continuous introduction of liquid aerosols. Moreover, the nitrogen plasma gas running costs are much lower than those of the Ar-ICP. Recently, the excitation temperature and electron density of a high power N_2-MIP were reported [9, 10, 11]. The wide use of this excitation source can be expected, so a detailed study of the matrix effect will be reported. By the way, quite a few applications of the high power N_2-MIP as an excitation source for atomic emission spectrometry (AES) were performed for the determination of trace elements in a variety of real samples [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22,

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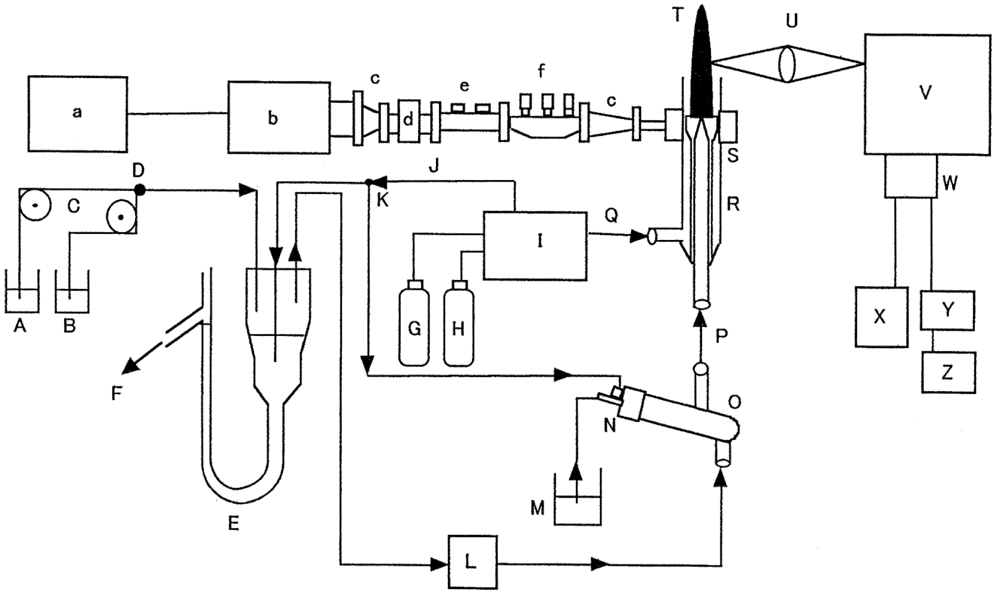

Fig. 1 Schematic diagram of high power N_2-MIP-AES system. *A*: sample solution for hydride generation, *B*: $NaBH_4$ solution, *C*: peristaltic pump, *D*: mixing joint, *E*: gas–liquid separator, *F*: waste, *G*: nitrogen tank, *H*: argon tank, *I*: gas controller, *J*: carrier gas, *K*: three-way stopcock,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

23, 24, 25]. Trace concentrations of bismuth and tellurium can affect the physical and mechanical properties of metals and metal alloys. Therefore, a sensitive technique is required for the determination of bismuth and tellurium in such samples. Generally, the hydride generation technique coupled with analytical atomic spectrometry is a sensitive analytical tool for the determination of trace elements in the IVa–VIa groups [26, 27, 28, 29].

In this paper, the feasibility of using a high power N_2-MIP for AES in the determination of bismuth and tellurium in combination with both a conventional solution nebulization and a hydride generation system is described. Their analytical figures of merit for bismuth and tellurium were obtained by sample introduction methods. After an interference study, the proposed method coupled with hydride generation was applied to the simultaneous determination of trace amounts of bismuth and tellurium in steels.

Experimental

Instrumentation and apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1 and the major instruments used in this work are listed in Table 1. Microwave power is transferred from the magnetron (2.45 GHz, 1.0 kW) of a Nippon Kousyuha MKN-103-3S microwave power generator to the torch through a uniline, directional 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 ICP 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 was installed between a laboratory-made gas–liquid phase separator and a nebulization chamber to remove the water vapor produced during hydride generation.

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

Reagents

A stock standard solution (1,000 mg/l) of bismuth was prepared from high-purity metal (99.999%, Wako Pure Chemical Industries, Ltd., Osaka). Solutions of lower concentration were prepared by appropriate dilution of the stock solutions immediately before use. Stock standard solutions (1,000 mg/l) of tellurium(IV) and tellurium(VI) were prepared from potassium tellurite (Wako Pure Chemical Industries, Ltd., Osaka) and sodium tellurate (Wako Pure Chemical Industries, Ltd., Osaka), respectively. Solutions of lower concentration were prepared by appropriate dilution of the stock solutions immediately before use. As a reducing solution for hydride generation, 0.3% (w/v) sodium tetrahydroborate(III) solution was prepared by dissolving sodium tetrahydroborate(III) (Wako Pure Chemical Industries, Ltd., Osaka) in 0.3% (w/v) sodium hydroxide (Wako Pure Chemical Industries, Ltd., Osaka) solution just before use.

All other reagents and solutions used were of analytical reagent grade or the highest purity available. High-purity water (Milli-Q water) was obtained by passing distilled water through a Milli-Q ion-exchange and membrane filtering system (Millipore, Bedford, MA, USA) with 18 MΩ cm specific resistivity capability.

General procedure

An acidified sample solution or a standard solution of bismuth and tellurium (normally tellurium(IV), unless otherwise noted), and the sodium tetrahydroborate(III) solution were continuously introduced into a gas–liquid phase separator by using a peristaltic pump. The generated bismuth and tellurium hydrides (BiH_3, bismuthine, and TeH_2, hydrogen telluride), after being conveyed through a drying

Table 2 Optimized operating conditions for the simultaneous determination of bismuth and tellurium by high power N_2-MIP-AES with continuous-flow hydride generation

Plasma	
Wavelength (nm)	Bi I 195.389 Te I 200.200
Slit width (μm)	25
Slit height (mm)	2.0
Microwave forward power (W)	1,000
Plasma gas flow rate (l/min)	12.0
Carrier gas flow rate (l/min)	0.3
Vertical position for observation (mm) (above the top of the cavity)	4.0
Horizontal position for observation (mm)	0.0 (center)
Hydride generation	
Sample solution acidity (M in HCI)	1.0
Sample solution flow rate (ml/min)	8.3
$NaBH_4$ concentration[a] [% (w/v)]	0.3
$NaBH_4$ solution flow rate (ml/min)	9.7

[a] In 0.3% (w/v) NaOH solution

Table 3 Emission characteristics of major lines of bismuth (5 μg/ml) and tellurium (5 μg/ml) by high power N_2-MIP-AES with continuous-flow hydride generation

Wavelength (nm)		I_n[a]	I_n/I_b[a]	BEC[b]
Bi I	195.389	1.00	1.20	4.2
Bi I	206.170	0.19	0.41	12.2
Bi I	222.825	0.11	0.33	15.2
Bi I	223.061	0.06	0.20	25.0
Bi I	306.772	0.64	0.75	6.7
Te l	200.200	1.00	1.05	4.7
Te l	214.275	0.20	0.46	10.9
Te l	214.719	0.26	0.48	10.4
Te l	225.719	0.19	0.44	10.4

[a] Relative to I_n and I_n/I_b of Bi I 195.389 and Te I 200.200 nm
[b] Background equivalent concentration (μg Bi or Te/mI)

flask for removing the water vapor, were swept into the high power N_2-MIP source through the drain outlet of the conventional nebulizer chamber by a stream of nitrogen carrier gas. For a conventional solution nebulization method, either a sample solution aerosol or a standard solution aerosol of bismuth and tellurium was introduced directly into the high power N_2-MIP source through the conventional nebulizer chamber. The optimized experimental conditions used are summarized in Table 2. The optimized experimental conditions obtained for the conventional solution nebulization method are not given here. Some of the optimum operating conditions given in Table 2 will be discussed below.

Sample digestion

Approximately 1.0 g of a sample of "Carbon steels for minor elements determination Series C" issued by The Japan Iron and Steel Federation (JSS) was weighed accurately and transferred to a 50-ml beaker. Ten milliliters 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 digested solution was transferred into a 50-ml volumetric flask and diluted to the mark with Milli-Q water. Then 10-ml portions of the sample solution were transferred into 50-ml volumetric flasks. Various volumes of hydrochloric acid and L-ascorbic acid were added to the sample solutions, which were subsequently diluted to the mark with Milli-Q water to give final solutions containing 1 M and 1.5% (w/v), respectively. The resultant solutions were then introduced into the high power N_2-MIP with hydride generation for the determination of bismuth and tellurium.

Results and discussion

Optimization of experimental conditions

The effects of various operating parameters were examined individually to obtain a maximum line-to-background intensity ratio, I_n/I_b (I_n, net analyte emission intensity; I_b, background emission intensity) for bismuth and tellurium. The optimized parameters for hydride generation are summarized in Table 2. Some of these optimum operating conditions, such as selection of analytical line for bismuth and tellurium, and effect of concentration of sodium tetrahydroborate(III) solution and acid, will be discussed below.

Selection of analytical lines for bismuth and tellurium

The emission characteristics of major lines for bismuth and tellurium were investigated by the hydride generation method and the results obtained are shown in Table 3. As a consequence, the Bi I 195.389 and Te I 200.200 nm lines giving the largest I_n/I_b in the hydride generation method were used throughout as analytical lines.

Effect of concentration of sodium tetrahydroborate(III) solution

It is well known that the concentration of sodium tetrahydroborate(III) as a reductant used in the hydride generation method affects the signal intensities for bismuth and tellurium [26, 27, 28, 29]. Under alkaline conditions, various concentrations in the range 0.2–0.6% (w/v) sodium tetrahydroborate(III) were examined and optimized by the measurement of I_n and I_n/I_b for bismuth and tellurium. The results are shown in Fig. 2. As a consequence, 0.3% sodium tetrahydroborate(III) was chosen for subsequent studies in this work. Also, the optimized flow rate of the reductant is shown in Table 2.

Effect of concentration of acid

The concentrations of several acids used in the hydride generation method have an important effect on the signal intensities of bismuth and tellurium [26, 27, 28, 29]. The effects of 0.1–5.0 M hydrochloric and acetic acids or 0.1–2.0 M citric, malic, and tartaric acids were examined and optimized by the measurement of I_n and I_n/I_b for bismuth and tellurium. As a result, with an increase in concentration in the 0.1–1.0 M range of every acid, both I_n and I_n/I_b increased. In particular, the effect of hydrochloric acid in the range 0.1–5.0 M is shown in Fig. 3, where I_n

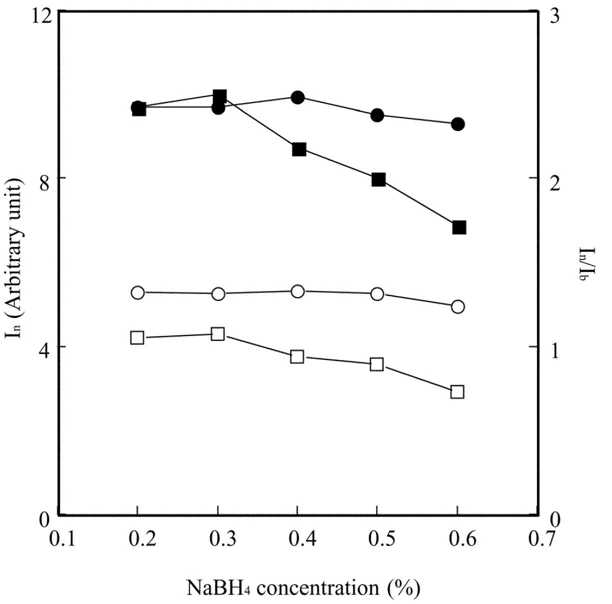

Fig. 2 Effect of $NaBH_4$ concentration on I_n for Bi (●) and for Te (■), and I_n/I_b for Bi (○) and for Te (□) with continuous-flow hydride generation

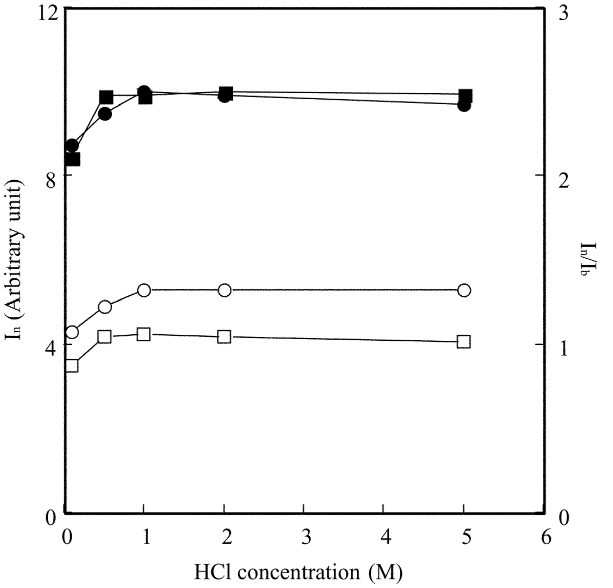

Fig. 3 Effect of HCl concentration on I_n and I_n/I_b for Bi (●) and for Te (■), and I_n/I_b for Bi (○) and for Te (□) with continuous-flow hydride generation

and I_n/I_b remained almost unchanged and became fairly high compared with other acids. As a consequence, 1.0 M hydrochloric acid was chosen for subsequent studies in the hydride generation method.

Prereduction step

Generally, tellurium exists in the oxidation states Te(IV) and Te(VI) under acidic solution conditions. The generation efficiencies of tellurium hydride from Te(IV) and Te(VI) are different in the hydride generation technique. Te(IV) solution gave a larger emission intensity than the same concentration of Te(VI), i.e., a ratio of intensity obtained from Te(VI) to that from Te(IV) was approximately 0.3 under the experimental conditions in Table 2. Therefore, Te(VI) must be reduced to Te(IV) prior to hydride generation for the determination of total tellurium [i.e., Te(IV)+Te(VI)]. In the present work, the use of potassium iodide, thiourea, L-cysteine, and L-ascorbic acid was evaluated. As a consequence, they were not found to be the most effective in the prereduction of Te(VI) to Te(IV). On the other hand, it is also well known that tellurium presents as Te(IV) in aqua regia solution [18, 30]. 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 was present as Te(IV) in aqua regia solution. Therefore, tellurium in steels dissolved in aqua regia was determined without the use of this prereduction procedure.

Analytical performance

Under the optimized operating conditions, double-logarithmic analytical working graphs were obtained for bismuth and tellurium by both conventional solution nebulization and the hydride generation technique with the use of freshly prepared bismuth and tellurium solutions. Detection limits for bismuth and tellurium 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) equal to three times the standard deviation of the background emission intensity. The detection limits for the simultaneous determination of bismuth and tellurium by high power N_2-MIP-AES coupled with hydride generation were 110 and 86 ng/ml with a linear dynamic range of 300–30,000 ng/ml, respectively, while the detection limits obtained by use of conventional solution nebulization were 4.12 and 1.57 μg/ml with the linear dynamic ranges of 10–1,000 and 3–1,000 μg/ml, respectively. Using the hydride generation method, the sensitivity for bismuth and tellurium was greatly improved. In the other methods, the detection limits for bismuth and tellurium were reported to be 0.06 and 0.04 ng/ml by hydride generation-ICP-AES [26] and 0.002 and 0.002 ng/ml by ICP-MS [31], respectively. The detection limits of the present high power N_2-MIP-AES method with hydride generation are much worse than those obtained by the other methods [26, 31]. Moreover, the detection limits of simultaneous determination for arsenic, antimony, and bismuth (three elements), and arsenic, antimony, bismuth, and selenium (four elements) by the same hydride generation high power N_2-MIP-AES method [32, 33] were found to be 7.13, 14.6, and 116, and 7.8, 14.5, 131, and 28.99 ng/ml, respectively. Also, the detection limits of single-element determination by same method [18, 34] for bismuth and tellurium were 102 and 15 ng/ml, respectively.

Table 4 Effect of diverse elements or ions on the simultaneous determination of bismuth and tellurium by high power N_2-MIP-AES with hydride generation

Element or ion[a]	Added as	Relative intensity[b]	
		Bismuth	Tellurium
As	As_2O_3	89.3	85.7
Cd	$Cd(N0_3)_2 \cdot 4H_20$	80.3	83.2
Co	Metal in HCI	86.7	75.9
Cr(VI)	$K_2Cr_2O_7$	88.9	–[c]
Cu	$CuSO_4 \cdot 5H_2O$	80.5	81.1
Fe(III)	$FeCl_3 \cdot 6H_2O$	79.8	73.1
Hg	$Hg_2(NO_3)_2$	82.7	–
Ni	$NiS0_4 \cdot 6H_20$	88.4	89.4
Pb	$Pb(NO_3)_2$	84.8	90.6
Pd	$PdCl_2$	–	87.3
Sb	$C_4H_4O_6KSbO \cdot 1/2H_2O$	83.4	79.5
Se	Na_2SeO_3	85.3	81.5
Sn	Metal in HCl	88.4	87.3
Ti	Metal in HCl	–	83.5
V	NH_4VO_3	81.6	–
W	$Na_2WO_4 \cdot 2H_2O$	75.9	86.7
Zn	Metal in HCl	88.1	91.3
Zr	$ZrO(NO_3)_2 \cdot 2H_2O$	80.8	–
BrO_3^-	$KBrO_3$	90.8	88.7
ClO_3^-	$NaCIO_3$	92.7	89.1
IO_3^-	KIO_3	–	80.3
NO_2^-	$NaNO_2$	90.3	82.6

[a] Diverse element or ion added at level of 1,000-fold ratio of bismuth and tellurium

[b] Relative to 100 for the emission intensity of bismuth and tellurium (μg/ml)

[c] No interference

Effect of diverse elements

The determination of bismuth and tellurium by hydride generation atomic spectrometry is well known to be susceptible to interferences from various diverse elements [26, 27, 28, 29]. Under the experimental conditions used here, the effect of various other elements on the determination of bismuth and tellurium by the present hydride generation high power N_2-MIP-AES system was examined. The depressing interferences from some elements are shown in Table 4. An interference is considered to have occurred when an emission intensity is changed by over ±5% from that for bismuth and tellurium. The following elements or ions at levels 1,000-fold greater than bismuth and tellurium did not interfere: Al, B, Ba, Be, Ce, Cr(III), Cs, Fe(II), Ga, Ge, In, K, Li, Mg, Mn, Mo, Na, P, Sr, Tl, Y, Br^-, Cl^-, $C_2O_4^{2-}$, F^-, NH_4^+, and SO_4^{2-}. The relative intensity is defined in Table 4 as the ratio of the bismuth or tellurium emission intensities obtained in the presence of the foreign element or ion to those obtained when no element or ion was present in the analyte solution. A number of elements interfere with the determination of bismuth and tellurium by the present technique. In particular, the presence of Fe(III) gave rise to a significant interference. The elimination of this interference will be mentioned later.

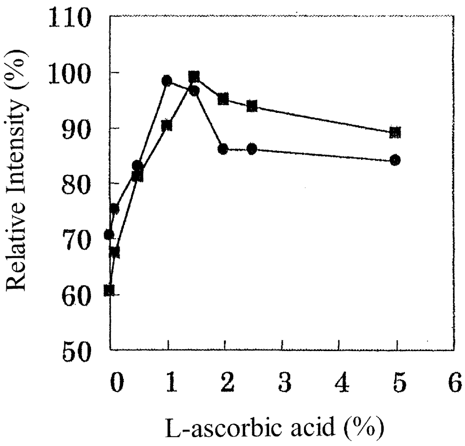

Fig. 4 Effect of L-ascorbic acid concentration on emission intensity of bismuth and tellurium in the presence of 5,000 μg Fe(III)/ml

Table 5 Simultaneous determination of bismuth and tellurium in steels by high power N_2-MIP-AES with hydride generation

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

[a] Carbon steels for minor elements determination Series C issued by The Japan Iron and Steel Federation

[b] The mean±standard deviation, based on 5five replicate determinations

Determination of bismuth and tellurium in steels

In order to validate the effectiveness of the present method for practical analysis, some certified standard reference materials of JSS were analyzed for bismuth and tellurium using the hydride generation high power N_2-MIP-AES technique. It was expected that Fe(III) as a major constituent of the steels, present at greater than 1,000-fold concentration ratio to bismuth and tellurium in the sample solutions, was likely to interfere with their determination by the proposed method, as previously shown in Table 4. However, as already mentioned, the presence of Fe(II) showed little or no significant interference. In other words, 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. For this purpose, the effects of 0.1–5.0% (w/v) of L-cysteine [18, 19, 32, 35, 36, 37, 38], 0.1–5.0% (w/v) of L-ascorbic acid [17, 22, 33, 34], and 0.05–0.5% (w/v) of thiourea [16, 20, 23, 24, 34, 37, 39, 40] were investigated as interference-releasing agents. The results showed that 1.5% of L-ascorbic acid was the most preferable in the prereduction of Fe(III) to Fe(II), as shown in Fig. 4. Therefore, a calibration graph method could be employed in the determination. Bismuth and tellurium were determined in three certified reference steel samples and the results calculated by least-squares analysis are presented in Table 5. The determined concentrations of bismuth and tellurium were in good agreement with the certified values.

Conclusions

It has been demonstrated that the present technique using a high power N_2-MIP, which is particularly a new one for plasma spectrochemical sources, can be used for the simultaneous determination of trace amounts of bismuth and tellurium in steels. The detection limits of this hydride generation high power N_2-MIP-AES system for bismuth and tellurium are greatly improved compared with conventional solution nebulization. This dramatic improvement in detection limit could make the determination of trace amounts of bismuth and tellurium by hydride generation high power N_2-MIP-AES practical for a wide range of samples, although the present detection limits are fairly poor compared to those obtained by the other corresponding methods [26, 31]. In addition, L-ascorbic acid appears to be very effective in eliminating or minimizing serious interferences from Fe(III) in the determination of bismuth and tellurium. The present method using L-ascorbic acid as an interference-releasing agent was successfully applied to the determination of low concentrations of bismuth and tellurium in steels. In short, this technique can be expected to remove the analyte from the matrix in a real sample, improving accuracy and giving rapid online preconcentration of the analyte. The application of this technique appears to be promising and its extension to other hydride-forming elements is currently under way in this laboratory.

Acknowledgements This work was supported in part by a Grant-in-Aid For Scientific Research (No. 13650872) from the Ministry of Education, Science, Sports and Culture of Japan.

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