Determination of ultra-trace tellurium in steel by ID-ICP-MS/MS with liquid-liquid extraction

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Abstract

Inductively coupled plasma mass spectrometry using isotope dilution (ID-ICP-MS) with liquid-liquid extraction was used for determining ultra-trace tellurium (Te) in steels to improve the sensitivity, accuracy, and precision of the analysis. Single quadrupole-type ICP-MS cannot be used to determine the trace amount of Te because of contribution of mass spectrometric interference by Xe. To overcome this, tandem mass-filter-type ICP-MS (ICP-MS/MS) was used for the determination of Te. Pretreatment by liquid-liquid extraction was also employed to compensate for the decrease in signal intensity due to the use of ICP-MS/MS. The relative standard deviations of the resulting abundances defined by repeated analysis from separated three steel samples were <1.3%. Furthermore, the determined values of Te in standard reference materials were close to the reference values. Thus, the developed determination method is useful for the analysis of ultra-trace Te in steels.

Keywords: Inductively coupled plasma mass spectrometry, Isotope dilution, Tellurium, Steel

Introduction

In steel industry, controlling trace elemental composition in steels is important for both the manufacture of high-quality and stable products. Controlling the elemental components of steel is difficult because various raw materials are used for the iron-making and steel-making processes. Recently, traditional raw materials such as coal, iron ore, and limestone, as well as recycled materials such as plastics and gums have been used for iron making^{1, 2}. The use of recycled scrapped steel in the steel-making process has also increased³. The elemental composition of these recycled raw materials is often unknown, and thus, the impurity elements in products must be determined to control the quality of steel products^{4,5}. Tellurium (Te) in steel is an impurity element that needs to be determined because trace Te in steel has an undesirable effect on the mechanical properties of products, such as ductility and brittle⁶⁻⁸. For example, undesirable Te can produce inclusions or segregate in the steel, which can cause the crack of the steel. Flameless atomic adsorption spectrometry (FLAAS) is the most commonly used method for the determination of ultra-trace Te in steels⁹. The limit of quantification (LOQ) of Te by FLAAS proposed by Japan Industrial Standard (JIS) is $2 \mu\text{g g}^{-1}$, and, the precision of FLAAS becomes poor when the Te content is close to the LOQ. Inductively coupled plasma-mass spectrometry (ICP-MS) is another method to determine ultra-trace Te in steels. ICP-MS is expected to be a precise method for low trace amounts of Te in steels^{10,11}. Despite this, there have been few reports on the determination of Te in steels by ICP-MS.

Various mass spectral interferences of Te have been extensively reported in previous reports^{12, 13}. Polyatomic ions containing molybdenum (Mo) and niobium (Nb) can cause analytical error in the determination of Te in steels, because Mo and Nb are commonly contained as micro-alloys¹⁴. It is also known that Xe ions, which can be

originating from air through engulfment, interfere with the mass spectrum of Te isotopes. The ICP-MS with a collision reaction cell (ICP-CRC-MS), high-resolution type ICP-MS (HR-ICP-MS), and ICP-tandem mass spectrometry (ICP-MS/MS) have been widely used to remove these mass spectral interferences. ICP-MS/MS has additional advantages, such as the ability to remove mass spectral interferences, ease of operation, or lower equipment costs compared with those of ICP-CRC-MS and HR-ICP-MS¹⁵. However, in the case of determining ultra-trace levels of Te in steels by ICP-MS/MS, the precision of the determined values becomes poor owing to deterioration of the elemental sensitivity of Te. Thus, it is necessary to develop a precise method for the determination of ultra-trace Te in steels.

The purpose of this study was to establish a precise and accurate determination method for ultra-trace concentrations (few micrograms per gram) of Te in steels. First, the performance of ICP-MS/MS using calibration curve method was investigated in terms of reliability and precision. A recovery test of ultra-trace Te in the presence of Mo and Nb was also conducted to investigate the effect of their mass spectral interferences on Te isotopes. Second, for a more precise determination of ultra-trace Te, isotope dilution (ID)-ICP-MS/MS method was developed. To select the best conditions for ID-ICP-MS, the signal intensities of Xe ions were compared under various operational conditions. Xe ions were measured under conditions of single-mass mode without the CRC gas (no-gas mode), single mass mode using He gas (He collision mode), and tandem mass filtering mode using O₂ gas (O₂ mass shift mode). The mass discrimination effect on Te isotopes was also investigated for the accurate determination of Te by ID-ICP-MS/MS. Finally, liquid-liquid extraction using 4-methyl-2-pentanone was applied in the pretreatment of steels to reduce the contribution of the decrease in signal intensity due to the use of the O₂ mass shift mode. The concentration of Te in the

standard reference materials (SRMs) for steels was determined by ID-ICP-MS/MS, the applicability of the developed method was verified.

Experimental

Reagents and samples

Single elemental standard solutions (Kanto Chemical Corporation, Japan) of Y and Te were used for the calibration of Te. Single standard solutions (Kanto Chemical Corporation, Japan) of Mo and Nb were used to examine the effects of polyatomic ions. Prime pure-grade nitric acid (HNO_3) for sample decomposition and sulfuric acid (H_2SO_4) for stocking Te in solutions were purchased from Kanto Chemical Corporation, Japan. The reagents used for liquid-liquid extraction were hydrochloric acid (HCl , prime pure-grade, Kanto Chemical Corporation, Japan), 4-methyl-2-pentanone (special-grade, Kanto Chemical Corporation, Japan), and potassium permanganate (KMnO_4 , 0.2 mol/L for volumetric analysis, Kanto Chemical Corporation, Japan). The reagent for spiking ^{125}Te for isotope dilution was purchased from ISOFLEX Corporation. The abundance of various Te isotopes in the spike sample are shown in Table 1 which are provided by the ISOFLEX. This reagent is metallic Te, therefore, the sample was decomposed by acids according to the procedure described later in this section. Ultrapure water (18.2 M Ω) was employed for all sample preparation. The concentration of the spike solution was determined by reverse isotope dilution method using ICP-MS/MS. The standard solution of Te containing natural isotopic abundance was used for the determination. The isotopic abundance of spike solution was measured using O_2 mass shift mode as shown in Table 1.

Electrolytic iron (purity >99.999%, MAIRON UHP, TOHO ZINC Corporation, Japan) was used for checking the blank, matrix matching of the standard solutions, and

tests of Te recovery. SRM 361, SRM 363, and SRM 364 provided by the National Institute of Standards and Technology (NIST) were employed as the actual steel samples. The major elemental components of the SRMs are shown in Table 2.

Instrumentation

An Agilent 8800 (Agilent Technologies Corporation, Japan) was used for all measurements in this study. The operating conditions of Agilent 8800 are listed in Table 3. Other parameters, such as torch positions and mass axis, were automatically tuned using the mass spectra of Li, Y, and Tl prior to the Te determinations. The gas flow rate of O₂ gas was set 30 % because increasing of signal intensity of TeO⁺ with increasing of O₂ gas flow rate was saturated around this gas flow rate. It was difficult to select the best He collision gas flow rate, because the more He gas removed not only the polyatomic ions but also objective ions. Therefore, He gas flow rate was set to be the signal intensity of ¹³⁰Te⁺ become more than 1000 cps for 5 ppb Te standard solution.

Preparation of matrix-matched standards of Te

Electrolytic iron was decomposed using HNO₃ according to the procedure proposed by Hayashi et al.¹⁶. Electrolytic iron (1 g) and diluted HNO₃ (30 mL) were added to a quartz beaker and gently heated on a hot plate. After decomposition of the electrolytic iron, the sample solutions were transferred to 100 mL of volumetric vessels. Standard solutions of Te (0, 0.05, 0.1, and 0.5 µg L⁻¹) containing 100 mg L⁻¹ of Fe were prepared for the determination of Te by calibration curve method. Te solutions (0.1 µg L⁻¹) containing 1 mg L⁻¹ of Mo or Nb and 100 mg L⁻¹ of Fe were prepared to investigate the interference of Fe, Mo, and Nb spectra with Te mass spectra. The ratios of these elements were similar to those in steels containing 1% (w/w) Mo or Nb.

Liquid-liquid extraction for ID-ICP-MS/MS

Figure 1 displays a schematic of Te determination by ID-ICP-MS in this study. The ^{125}Te spiking reagent for isotope dilution was decomposed by HNO_3 , and the spike solution was diluted with H_2SO_4 according to the method proposed by JIS⁹. The spike solution was diluted to approximately 5 mg kg^{-1} of Te solution, and the spike of ^{125}Te was added to the quartz beakers before the decomposition of the steels. The steel samples were decomposed by HNO_3 according to the procedure proposed by Hayashi et al.¹⁶ If any residue was observed in the decomposed sample, the residue was filtered away using a 5B filter paper (ADVANTEC Co.). Te in the residual fractions was negligible because Te in steel was contained as telluride metal such as FeTe and MnTe ^{6,7}, which were easily decomposed by nitric acids. It was expected that the residues were nitride, carbide, or oxide, which were difficult to decompose by HNO_3 ¹⁷. To minimize adsorptions of Te on the surface of the residue, the residues were rinsed by diluted HNO_3 after filtration. After diluting the sample solution in 100 mL volumetric flasks, 20 mL of the sample solutions were transferred to separatory funnels for liquid-liquid extraction.

The liquid-liquid extraction procedure was carried out according to the method proposed by JIS⁹. To oxidize Te^{4+} to Te^{6+} , KMnO_4 was added to each sample and left over 15 minutes until the color of the solution became purple. The sample solutions were mixed with HCl and 4-methyl-2-pentanone. The water phase was separated from the 4-methyl-2-pentanone phase after shaking the samples, where Fe and Mo were distributed in the 4-methyl-2-pentanone phase and Te was distributed in the water phase. The water phase was gently heated so that Te^{6+} could be reduced to Te^{4+} by Cl^- ions. 4-methyl-2-pentanone and HCl were added to the separatory funnels again, and the water phase was removed after the extraction of Te^{4+} into the 4-methyl-2-pentanone

phase. Ultra-pure water was added to the separatory funnels for the back extraction of Te^{4+} into the water phase. After the removal of the 4-methyl-2-pentanone phase, the water phase was gently heated on a hot plate to vaporize the remaining 4-methyl-2-pentanone in the water phase. The water phase containing Te^{4+} was added to 25 mL of volumetric flasks. The pretreated SRMs were measured by ICP-MS/MS. Recovery tests were also performed to validate the correctness of the analytical procedure using ID-ICP-MS and liquid-liquid extraction. In the case of the Te recovery test, 1 μg of Te was added to the quartz beaker before the decomposition of electrolytic iron. The samples for the recovery tests were measured using no-gas mode, He collision mode, and O_2 mass shift mode to compare the accuracy of the determined values of Te in each mode.

In the above oxidation step using KMnO_4 , all of the Te^{4+} must be oxidized to achieve isotope equilibrium. To check the oxidation rate, pre-experiment was performed. Reagent of TeCl_4 was dissolved in ultra-pure water, and KMnO_4 was added to the sample. Te in the resulting sample solution was extracted by 4-methyl-2-pentanone after adjusting of HCl concentration, and the concentration of Te in the water phase was determined by ICP-MS. Because more than 99 % of Te was distributed in water phase, it is concluded that Te ion in solution was only Te^{6+} .

Determination of Te in steels by ID-ICP-MS/MS

The obtained signal intensities were converted to Te concentrations using equation (1)¹⁸.

$$C_x = C_{\text{spike}} \times \frac{m_{\text{spike}}}{m_x} \times \frac{A_{\text{spike}} - R_{\text{mix}} \times B_{\text{spike}}}{R_{\text{mix}} \times B_x - A_x}, \quad (1)$$

where C_x is the molar concentration of Te in an objective sample, C_{spike} is the molar

concentration of Te in the spike solution, m_x is the weight of the objective sample solution, and m_{spike} is the molar of the spike solution. A_{spike} and B_{spike} are the isotopic abundances of isotopes A and B in the spike solution, respectively. A_x and B_x are the isotopic abundances of isotopes A and B in an objective sample, and R_{mix} is the isotopic ratio of isotopes A and B in the objective sample solution mixed with the Te spike solution. The measured signal intensities (I_{measur}) were corrected for the counting loss due to detector dead time based on equation (2)^{18,19}.

$$I_{\text{true}} = \frac{I_{\text{measur}}}{1 - \tau \times I_{\text{measur}}} \quad (2)$$

Where, I_{ture} was the signal intensity after dead time correction, and τ was the dead time. The value of τ was 31.8 ns according to the previous study²⁰, which was adjusted value by manufacturer. The concentration of Te in spike solution was recalibrated by the reverse isotope dilution (RID) method using following equation (3)²¹.

$$C_{\text{spike}} = C_{\text{std}} \times \frac{m_{\text{std}}}{m'_{\text{spike}}} \times \frac{R_{\text{std}} - R'_{\text{mix}}}{R'_{\text{mix}} - R_{\text{spike}}} \quad (3)$$

C_{spike} and C_{std} are the molar concentration of Te in the spike and standard of Te, m'_{spike} and m_{std} are the weights of the spike and standard solutions, R_{spike} and R_{std} are the measured isotope ratios of isotope A and B for the spike and the standard solutions, R'_{mix} was the measured isotope ratios of isotope A and B for the solution mixing the spike and standard solution.

Isotopic abundance of Te isotopes in the spike solution was measured by the ICP-MS/MS (Table 1), and the values were substituted in equation (1) and (3). ¹²⁵Te and ¹²⁸Te were used for the determination using the ID and RID methods. The mixing ratio of the spike solution and the steel sample was adjusted based on ¹²⁵Te¹⁶O⁺. Based on

previous study¹⁸, the signal intensity of $^{125}\text{Te}^{16}\text{O}^+$ from 50000 to 100000 cps was preferable for precise determination of Te, when the concentration of Te was low. Therefore, mixing ratio was adjusted to follow the instruction, as well as possible. For the determination of spike solution, signal intensities of $^{125}\text{Te}^{16}\text{O}^+$ and $^{128}\text{Te}^{16}\text{O}^+$ were adjust to be about 200000 to 300000 cps, according to the instruction by Inagaki¹⁸.

Results and Discussion

Evaluation of determination of Te by ICP-MS/MS using calibration curve method

The choice of Te isotopes for the isotope ratio measurement was key issue to avoid the erroneous measurements due to various mass spectral interferences, as shown in Table 4^{12,13,22}. A recovery test of ultra-trace Te was conducted to examine the effect of the mass spectral interferences. Te solutions (0.1 µg L⁻¹) were measured using the three modes, and each measurement was performed three times. The recoveries were calculated using Equation (4). If the recovery exceeds 100%, it is considered that mass spectral interference affects the recovery because of an increase in signal intensity derived from other matrices.

$$\text{Recovery (\%)} = \frac{\text{Determined weight of Te by measurement (g)}}{\text{Added weight of Te (g)}} \times 100 \quad (4)$$

As shown in Table 5 (a), the RSDs of the recoveries in the no-gas mode were 2.1–6.2%. The RSDs obtained by He collision and O₂ mass shift modes were exceeded this range because of a lowering signal intensities due to the collision-induced scattering effect. The Te in the Fe matrix was accurately determined by each condition. The 0.1 µg L⁻¹ of Te in the solution containing 100 mg L⁻¹ of Fe and 1 mg L⁻¹ of Mo or Nb was also determined by the calibration curve method three times to examine the effect of polyatomic ions from matrix elements in steels. As shown in Table 6 (b), the recoveries in the no-gas mode exceeded 100%. In contrast, 100% of Te was recovered within the 2σ under the other conditions. These results suggest that the polyatomic ions generated from Mo can be removed by He collisions or O₂ gas reactions. The recovery of ¹²⁵Te in the no-gas mode in Table 5 (b) exceeded 100% because of the contribution of Mo-related mass spectrometric interferences on 125 Da. It was assumed that the species

of interference ions were $^{92}\text{Mo}^{16}\text{O}_2^+\text{H}^+$ and $^{97}\text{Mo}^{14}\text{N}_2^+$. For Nb solutions, the recoveries at m/z values of 125 and 126 exceeded 100%, as shown in Table 5 (c). The mass spectral interference at m/z values of 125 was $^{93}\text{Nb}^{16}\text{O}_2^+$, as reported in a previous study¹¹, and the mass spectral interference at m/z values of 126 was newly identified in this study. Although the interference at $m/z = 126$ by Nb was not specifically identified, $^{93}\text{Nb}^{16}\text{O}_2^+\text{H}^+$ could be the interfering species. The interferences by Nb and Mo were removed in the O_2 mass shift mode. In contrast, in the He collision mode, the interference by MoO_2^+ was removed, whereas the interference by $^{93}\text{Nb}^{16}\text{O}_2^+$ could not be removed (Table 5 (b)). The degree of mass spectral interference of $^{93}\text{Nb}^{16}\text{O}_2^+$ onto $^{125}\text{Te}^+$ was greater than that of MoO_2^+ with $^{125}\text{Te}^+$. Thus, it was revealed that the O_2 mass shift mode is a powerful protocol for the removal of the mass spectral interferences of Mo and Nb. However, it was also revealed that precise determination of Te is difficult using the O_2 mass shift mode. A precise method for the determination of ultra-trace Te in steels is still lacking. The data obtained here revealed that isolation of the Te through the chemical separation procedures, such as liquid-liquid extraction, are effective to improve both the precision and accuracy of the Te analysis.

Examination of interference by Xe ions and mass discrimination effects of Te isotopes

For the precise determination of ultra-trace Te in steels, determination by ID is the preferred technique. The accurate determination of Te by ID-ICP-MS is difficult because of the mass spectral interference by Xe ions and the mass discrimination effect among Te isotopes.

ID-ICP-MS requires two different interference-free isotopes; however, Xe ions contained in air interfere with the mass spectra of $^{126}\text{Te}^+$, $^{128}\text{Te}^+$, and $^{130}\text{Te}^+$, which were relatively major Te isotopes. The background intensity was compared to examine the

mass spectral interference caused by Xe ions. Fig. 2 shows the signals of Te isotopes obtained by each ICP-MS condition. The signals obtained in the no-gas and He collision modes were in good agreement with the natural isotopic abundance of Xe ions. The Xe ions were not removed selectively by the He collision mode. Mono atomic ions (Te^+ and Xe^+) were less removed by He collision than polyatomic ions such as MoO_2^+ and NbO_2^+ , because of the difference of collision probability. However, the abundance by the O_2 mass shift mode was evidently different from the natural isotopic abundance of Xe.

The ions of Te^+ and Xe^+ could be separated by the difference in reactivity with O_2 gas. The bimolecular reaction in the reaction cell is expressed as equation (5) and (6)^{23,24}.

$$\Delta_r H = D_0(\text{O}_2) - D_0(\text{M}^+-\text{O}) \quad (6)$$

$D_0(\text{O}_2)$ and $D_0(\text{M}^+-\text{O})$ are the bond dissociation energy of O_2 and MO^+ , $\Delta_r H$ is the enthalpy of the bimolecular reaction. The reaction between an ion (M^+) and O_2 gas in the reaction cell proceed, when enthalpy ($\Delta_r H$) was bellow or nearby zero. The values of dissociation energy of Xe^+ and Te^+ were not reported as far as we know^{24,25}. However, $\Delta_r H$ of Ar^+ which is a noble gas as the same as Xe^+ , and $\Delta_r H$ of S^+ and Se^+ which are the chalcogens as the same as Te^+ , were reported by the previous studies. It was reported that Ar^+ was not react with O_2 gas because the $\Delta_r H$ was positive value, and S^+ and Se^+ were react with O_2 gas because the $\Delta_r H$ of S^+ was less than zero, and the $\Delta_r H$ of Se^+ was close to zero. Thus, Xe^+ could react with O_2 gas not so much, and Te^+ react with O_2 gas in the CRC. Mass spectral interference by Xe ions could be almost completely removed in the O_2 mass shift mode due to the difference of the bond dissociation energy between Xe^+ and Te^+ .

It is generally known that a mass discrimination effect causes bias in isotope ratio

analysis^{18,26,27}. The standard solution of Te with natural isotopic abundance was analyzed by ICP-MS/MS to examine the effect of the mass discrimination. 25 µg g⁻¹ of Te solution was measured because the signal intensity of ¹²⁸Te¹⁶O⁺ was close to the signal intensity of the recovery test and steel samples. The measured RSDs by ICP-MS/MS were 2.66 to 4.82 (Table 6), suggesting that changes of the mass discrimination effect could not be detected by the present operating conditions and system set up used for this study. There is a possibility to detect the mass discrimination effect, when higher concentration of Te standard solution is measured. However, the use of high concentration of Te standard solutions for the correction of the mass discrimination effect by comparison method can cause another problem. The memory of the sample introduction tube has to be washed out completely for the determination of ultra-trace tellurium, which is highly time-consuming. On the other hand, it is known that the correction factor is slightly varied during the analysis¹⁸. This point seemed the common and difficult problem in the field of the determination of ultra-trace elements by ID-ICP-MS/MS. The selection of the mass bias correction method^{28,29}, such as comparison method, internal correction method, or external correction method was expected to be examined by further research.

The mass discrimination effect on Te isotopes were not considered for the determination of Te in this study, because the effects of mass discrimination were smaller than analytical uncertainties achieved in this study. Even though the measured value of ¹³⁰Te/¹²⁵Te was agree within 2σ with the natural isotopic abundance, ¹³⁰Te/¹²⁵Te might be slightly higher than the natural isotopic abundance. ¹²⁸Te/¹²⁵Te was used for ID-ICP-MS in this study to minimize the effect of mass discrimination effect, because the natural isotopic abundance of ¹²⁸Te was the second largest.

Determination of Te in steels by ID-ICP-MS/MS with liquid-liquid extraction

As shown in Tables 5, the RSDs by the O₂ mass shift mode using calibration curve method were not sufficient for the precise determination of Te because of a decreased signal intensity. A pre-concentration of Te through the liquid-liquid extraction technique was applied in the present ID-ICP-MS/MS to improve both the signal-to-noise ratio and precision of the signals. The results of recovery tests by ID-ICP-MS after liquid-liquid extraction are shown in Table 7. The recoveries of Te obtained with no-gas mode and He collision mode exceeded 100% because of mass spectral interference by Xe ions. The recoveries of Te in the O₂ mass shift mode were close to 100%. Furthermore, the RSDs obtained by the analysis from separated three steel samples was 0.52 %, which is better than those obtained using the calibration curve method shown in Table 5 (a).

Finally, Te contents in the SRMs were determined by the developed method, as shown in Table 8. Te values determined by ID-ICP-MS/MS with liquid-liquid extraction are close to the reported values provided by NIST. Furthermore, the RSDs of SRM 361, SRM 363, and SRM 364 were 0.78, 0.51, and 1.3%, respectively. These results are remarkable, considering that the experiment was performed independently from sample preparation to measurement. Thus, it is confirmed that ID-ICP-MS/MS with pretreatment by liquid-liquid extraction can be used for the accurate and precise determination of ultra-trace Te in steels.

Conclusion

ID-ICP-MS/MS with liquid-liquid extraction is proposed to achieve a precise and accurate determination of ultra-trace Te in steels. This study revealed the following:

- (1) The mass spectral interference by Xe ions was almost completely removed in the O₂ mass shift mode by ICP-MS/MS, which was advantageous for the determination of Te

by ID.

(2) The RSDs by ID-ICP-MS/MS after liquid-liquid extraction were 0.51-1.3 %, better than those obtained by ICP-MS with the calibration curve method.

(3) Te added to electrolytic iron was recovered by almost 100% by the developed method, and the determined values of Te in SRMs were close to the values reported by NIST.

Thus, the validity and superiority of the proposed method are confirmed. The developed method for ultra-trace Te determination in steels will facilitate the stable production of high-quality steel.

References

1. J. R. Dankwah, P. Koshy, N. M. Saha-chaudhury, P. O'kane, C. Skidmore, D. Knights, and V. Sahajwalla, *ISIJ Int.*, **2011**, *51*, 498.
2. H. Kuwatori, *Tetsu-to-Hagane*, **2014**, *100*, 59.
3. C. Ryman and M. Larsson, *ISIJ Int.*, **2006**, *46*, 1752.
4. K. Fujimoto, M. Shimura, and S. Satoh, *Tetsu-to-Hagane*, **2002**, *88*, 285.
5. H. Naka and T. Nakahara, *Tetsu-to-Hagane*, **2014**, *100*, 857.
6. D. Bhattacharya and D. T. Quinto, *Metall. Trans. A*, **1980**, *11A*, 919.
7. T. Shiraga and Y. Shingaki, "Tekkouzairyou to goukingenso (Steels and alloying elements, in Japanese)", ed. M. Enomoto, 2015, Chap. 29, Iron and steel institute of Japan, Tokyo.
8. Z. Takao, *Bunseki Kagaku*, **1967**, *16*, 1104.
9. JIS G 1257-18-2, "Iron and steel-Atomic absorption spectrometric method-Part 18: Determination of tellurium-Section 2: Electrothermal atomization", 2013, Japanese Industrial Standards Committee, Tokyo.
10. K. Fujimoto, M. Shimura, and S. Satoh, *ISIJ Int.*, **2002**, *43*, 101.
11. G. Okano, S. Igarashi, O. Ohno, Y. Yamamoto, S. Saito, and Y. Oka, *ISIJ Int.*, **2015**, *55*, 332.
12. J. Hu and H. wang, *Microchim. Acta*, **2001**, *137*, 149.
13. T. W. May and R. H. Wiedmeyer, *Atom. Spectrosc.*, **1998**, *19*, 150.
14. H. Mohrbacher, *Metals*, **2018**, *8*, 234.
15. L. Balcaen, E. B. Fernandez, M. Resano, and F. Vanhaecke, *Anal. Chim. Acta*, **2015**, *894*, 7.
16. K. Hayashi and T. Ogata, *Bunseki Kagaku*, **1966**, *15*, 1120.

17. Y. Yoshida and I. Kanji, *Bunseki Kagaku*, **1979**, 28, 733.
18. H. Tao, Y. Iida, K. Inagaki, J. Takahashi, and T. Nakazato, “*Yudoketsugo plasma shitsuryo bunseki* (Inductively coupled plasma mass spectrometry, in Japanese)”, ed. H. Haraguchi, H. Ishida, H. Ohtani, T. Suzuki, H. Seki, and H. Watarai, Kyoritsushuppan, Tokyo, 160.
19. S. M. Nelms, C. R. Quétel, T. Prohaska, J. Vogl, and P. D. P. Taylor, *J. Anal. At. Spectrom.*, **2001**, 16, 333.
20. A. Gourgiotis, T. Ducasse, E. Barker, P. Jollivet, S. Gin, S. Bassot, C. Cazala, *Anal. Chim. Acta*, **2017**, 954, 68.
21. N. Nonose, A. Hioki, M. Kurahashi, and M. Kubota, *Bunseki Kagaku*, **1998**, 47, 239.
22. J. Meija, T. B. Coplen, M. Berglund, W. A. Brand, P. D. Bivère, M. Gröning, N. Holden, J. Irrgeher, R. D. Loss, T. Walczyk, and T. Prohaska, *Pure Appl. Chem.*, **2016**, 88, 293.
23. N. Yamada and J. Takahashi, *Bunseki Kagaku*, **2018**, 67, 249.
24. G. K. Koyanagi, D. Caraiman, V. Blagojevic, and D. K. Bohme, *J. Phys. Chem. A.*, **2002**, 106, 4581.
25. T. Narukawa and K. Chiba, *Anal. Sci.*, **2013**, 29, 747.
26. A. J. Walder and I. Platzner, *J. Anal. At. Spectrom.*, **1993**, 8, 19.
27. L. Yang, S. Tong, L. Zhou, Z. Hu, Z. Mester, and J. Meija, *J. Anal. At. Spectrom.*, **2018**, 33, 1849.
28. T. Hirata, *Bunseki Kagaku*, **1996**, 45, 465.
29. Y. Shimamura and I. Nakai, *Bunseki Kagaku*, **2013**, 62, 774.

Table 1 Isotopic abundances of spike solution

(% : w/w)

		¹²⁰ Te	¹²² Te	¹²³ Te	¹²⁴ Te	¹²⁵ Te	¹²⁶ Te	¹²⁸ Te	¹³⁰ Te
Measured*	No 1	n. d.	n. d.	n. d.	0.033	99.79	0.040	0.0011	0.13
	No 2	n. d.	n. d.	n. d.	0.037	99.79	0.037	0.0012	0.13
	No 3	n. d.	n. d.	n. d.	0.034	99.80	0.042	0.0006	0.12
	Average	n. d.	n. d.	n. d.	0.035	99.80	0.040	0.0010	0.13
	± σ				± 0.002	± 0.01	± 0.002	± 0.0003	± 0.01
ISOFLEX**		0.01	0.01	0.01	0.04	99.75	0.05	0.01	0.12

*The spike solution was measured three times by ICP-MS/MS using O₂ mass shift mode. The isotopic abundances were calculated by [Signal intensity of a Te isotope] ÷ [Sum of the signal intensity of all of the Te isotopes] × 100. The error ranges for the average values were standard deviations.

**The values were provided by the ISOFLEX Corporation, where error ranges of the values were not given.

Table 2 Major elemental components in SRMs

(% : w/w)

	C	Si	Mn	P	S	Nb	Mo
SRM 361	0.383	0.222	0.66	0.014	0.0143	0.022	0.19
SRM 363	0.62	0.74	1.50	0.029	0.0068	0.049	0.028
SRM 364	0.87	0.065	0.255	0.01	0.0250	0.157	0.49

*The values were certified reference values provided by the NIST.

Table 3 Operating conditions of Agilent 8800 ICP-MS

Operating conditions	
RF power (W)	1550
Carrier gas (L min ⁻¹)	1.08
Skimmer cone	Ni cone for X lens
Sampling cone	Ni cone for X lens
Selected mass-charge ratio for No-gas mode and He collision mode	Te (125, 126, 128, 130), Y (89)
	1 st mass filter:
Selected mass-charge ratio for	Te (120, 122, 123, 124, 125, 126, 128, 130)
O ₂ mass shift mode	2 nd mass filter:
	TeO (136, 138, 139, 140, 141, 142, 144, 146)
Dwell time (ms)	500
Mass scan times (scan)	10
Total integration time (s)	5

Table 4 Mass spectral interferences and natural isotopic abundance of Te isotopes^{12,13,22)}

Isotopes interfered	Abundance Te (%)	Major interferences
¹²⁵ Te	7.07	⁹³ Nb ¹⁶ O ₂ ⁺
¹²⁶ Te	18.84	⁹⁴ Mo ¹⁶ O ₂ ⁺ , ¹¹⁰ Pd ¹⁶ O ⁺ , ¹²⁶ Xe ⁺
¹²⁸ Te	31.74	⁹⁶ Mo ¹⁶ O ₂ ⁺ , ⁹⁶ Ru ¹⁶ O ⁺ , ⁹³ Nb ³⁵ Cl ⁺ , ¹²⁸ Xe ⁺
¹³⁰ Te	34.08	⁹⁸ Mo ¹⁶ O ₂ ⁺ , ⁹⁸ Ru ¹⁶ O ₂ ⁺ , ¹³⁰ Xe ⁺ , ¹³⁰ Ba ⁺

Table 5 (a) Recoveries of 0.1 $\mu\text{g L}^{-1}$ of Te in Fe solutions.

(unit: %)

Isotope measured	Sample numbers and the average values	Conditions of mass filter and CRC		
		No-gas mode	He collision mode	O ₂ mass shift mode
¹²⁵ Te	No. 1	103	90.4	92.1
	No. 2	107	65.5	118
	No. 3	102	103	126
	Average $\pm \sigma$	104 $\pm$ 2	86.2 $\pm$ 19	112 $\pm$ 18
	(RSD %)	(2.1)	(22)	(16)
¹²⁶ Te	No. 1	105	97.8	82.4
	No. 2	115	94.5	114
	No. 3	117	111	110
	Average $\pm \sigma$	112 $\pm$ 6	101 $\pm$ 9	102 $\pm$ 17
	(RSD %)	(5.5)	(8.5)	(17)
¹²⁸ Te	No. 1	98.0	106	121
	No. 2	110	104	101
	No. 3	108	116	123
	Average $\pm \sigma$	105 $\pm$ 6	109 $\pm$ 6	115 $\pm$ 12
	(RSD %)	(6.2)	(5.9)	(10)
¹³⁰ Te	No. 1	98.9	92.7	92.5
	No. 2	110	116	121
	No. 3	110	103	96.9
	Average $\pm \sigma$	106 $\pm$ 6	104 $\pm$ 11	103 $\pm$ 15
	(RSD %)	(5.9)	(11)	(15)

*Recoveries were calculated as [determined weight of Te] / [added weight of Te] $\times$ 100.

** The samples were prepared from separated three electrolytic iron. The average values, the standard deviations (σ), and the relative standard deviations (RSDs %) were calculated from the determined values of the three samples.

Table 5 (b) Recoveries of 0.1 $\mu\text{g L}^{-1}$ of Te in Fe and Mo solutions

(unit: %)

Isotope measured	Sample numbers and the average values	Conditions of mass filter and CRC		
		No-gas mode	He collision mode	O ₂ mass shift mode
¹²⁵ Te	No. 1	116	91	141
	No. 2	113	102	95
	No. 3	115	79	60
	Average $\pm \sigma$	115 $\pm$ 1	91 $\pm$ 11	99 $\pm$ 41
	(RSD %)	(1.3)	(13)	(41)
¹²⁶ Te	No. 1	137	99.0	87.0
	No. 2	150	115	78.3
	No. 3	161	116	94.0
	Average $\pm \sigma$	149 $\pm$ 12	110 $\pm$ 10	86.4 $\pm$ 7.8
	(RSD %)	(8.3)	(8.8)	(9.1)
¹²⁸ Te	No. 1	131	97.0	98.3
	No. 2	151	105	93.4
	No. 3	163	108	99.4
	Average $\pm \sigma$	149 $\pm$ 16	103 $\pm$ 6	97.0 $\pm$ 3.2
	(RSD %)	(11)	(5.3)	(3.3)
¹³⁰ Te	No. 1	141	103	100
	No. 2	163	101	89.1
	No. 3	177	123	108
	Average $\pm \sigma$	160 $\pm$ 18	109 $\pm$ 12	99.2 $\pm$ 9.6
	(RSD %)	(11)	(11)	(9.7)

Table 5 (c) Recoveries of 0.1 $\mu\text{g L}^{-1}$ of Te in Fe and Nb solution

(unit: %)

Isotope measured	Sample numbers and the average values	Conditions of mass filter and CRC		
		No-gas mode	He collision mode	O ₂ mass shift mode
¹²⁵ Te	No. 1	233	272	136
	No. 2	245	193	117
	No. 3	242	217	97.3
	Average $\pm \sigma$	240 $\pm$ 6	227 $\pm$ 40	117 $\pm$ 19
	(RSD %)	(2.7)	(18)	(17)
¹²⁶ Te	No. 1	120	134	101
	No. 2	113	106	81.3
	No. 3	110	123	99.3
	Average $\pm \sigma$	114 $\pm$ 6	121 $\pm$ 14	93.9 $\pm$ 11
	(RSD %)	(4.8)	(12)	(12)
¹²⁸ Te	No. 1	117	120	115
	No. 2	111	114	102
	No. 3	106	107	100
	Average $\pm \sigma$	111 $\pm$ 6	113 $\pm$ 7	106 $\pm$ 8
	(RSD %)	(5.0)	(5.8)	(7.9)
¹³⁰ Te	No. 1	116	113	91.1
	No. 2	112	103	118
	No. 3	104	101	102
	Average $\pm \sigma$	110 $\pm$ 6	106 $\pm$ 6	104 $\pm$ 14
	(RSD %)	(5.6)	(6.0)	(13)

Table 6 Examination of mass discrimination effect on Te isotopes²²

Sample numbers		$^{126}\text{Te}/^{125}\text{Te}$	$^{128}\text{Te}/^{125}\text{Te}$	$^{130}\text{Te}/^{125}\text{Te}$
Measured	No. 1	2.66	4.59	5.00
	No. 2	2.66	4.38	4.84
	No. 3	2.65	4.41	5.05
	Average $\pm \sigma$	2.66 ± 0.01	4.46 ± 0.12	4.96 ± 0.11
	(RSD %)	(0.30)	(2.6)	(2.3)
Natural isotopic abundance		2.66	4.49	4.82

* The error range of measured isotopic abundance ratio is expressed as standard deviation (σ).

Table 7 Recovery test by ID-ICP-MS and ID-ICP-MS/MS after liquid-liquid extraction

(unit: %)

Sample numbers	Conditions of mass filter and CRC		
	No-gas mode	He collision mode	O ₂ mass shift mode
No. 1	102	117	98.9
No. 2	101	116	99.5
No. 3	102	119	99.9
Average $\pm \sigma$	101 $\pm$ 1	117 $\pm$ 1	99.4 $\pm$ 0.5
(RSD %)	(0.55)	(1.1)	(0.52)

*Recoveries were calculated as [determined weight of Te] / [added weight of Te] $\times$ 100.

** The error ranges are expressed by standard deviations (σ), and the values in the parentheses are the RSD values (%) obtained by three individual determinations of the recovery test.

Table 8 Determination of Te in SRMs by ID-ICP-MS/MS

(unit: $\mu\text{g g}^{-1}$)

	SRM 361	SRM 363	SRM 364
No. 1	5.31	10.0	1.81
No. 2	5.25	9.95	1.77
No. 3	5.23	10.1	1.81
Average $\pm \sigma$	5.26 $\pm$ 0.04	10.0 $\pm$ 0.05	1.80 $\pm$ 0.02
(RSD %)	(0.78)	(0.51)	(1.3)
Reported value	6	9	2

*The error ranges are expressed by standard deviations (σ), and the values in the parentheses are the RSD values (%) obtained by three individual determinations of the recovery test.

Figure Captions

Fig. 1 Liquid-liquid extraction procedure by 4-methyl-2-pentanone.

Fig. 2 Examination of mass spectral interference by Xe ions

Fig. 1

Fig. 2

Graphical Index

**Determination of tellurium in steel samples
by ID-ICP-MS/MS with liquid-liquid extraction**