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Rapid and sensitive determination of tellurium in soil and plant samples by sector-field inductively coupled plasma mass spectrometry

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ABSTRACT

In this work, we report a rapid and highly sensitive analytical method for the determination of tellurium in soil and plant samples using sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). Soil and plant samples were digested using *Aqua regia.* After appropriate dilution, Te in soil and plant samples was directly analyzed without any separation and preconcentration. This simple sample preparation approach avoided to a maximum extent any contamination and loss of Te prior to the analysis. The developed analytical method was validated by the analysis of soil/sediment and plant reference materials. Satisfactory detection limits of 0.17 ng g^{-1} for soil and 0.02 ng g^{-1} for plant samples were achieved, which meant that the developed method was applicable to studying the soil-to-plant transfer factor of Te. Our work represents for the first time that data on the soil-to-plant transfer factor of Te were obtained for Japanese samples which can be used for the estimation of internal radiation dose of radioactive tellurium due to the Fukushima Daiichi Nuclear Power Plant accident.

1. Introduction

Large amounts of radioactive tellurium (Te) were released into the environment due to the Fukushima Daiichi Nuclear Power Plant (DNPP) accident in March 2011 [1]. Among the released radioactive Te isotopes, ^{127m}Te, a beta emitter, may have posed a potential risk of internal radiation via crop ingestion because of its relatively long half-life ($T_{1/2}=109$ days). To accurately estimate the internal radiation dose, data of soil-to-plant transfer factor (TF) of Te are requisite. However, only five TF values of Te in temperate environment are reported in IAEA-TRS-472 (0.1–1.0) [2], and no data on the TF of radioactive Te are available for Japan. A useful approach to obtain the soil-to-plant transfer factor is the use of stable Te as an analog of radioactive Te; this requires a sensitive analytical method for Te determination because of the low concentration of Te in soil and plant samples.

As a result of its preferential sequestration into the Earth's core [3], the concentrations of Te in the environment are extremely low. An average abundance of 27 ng g^{-1} tellurium in soil has been estimated based on samples from Australia, China, Europe, New Zealand and North America [4]. In Japanese soil samples, concentrations of Te were reported to be in the range of 10–109 ng g^{-1} [5]. Terashima [6] also reported Te contents in 38 geological reference materials (soil and rocks) from the Geological Survey of Japan (GSJ) ranging from <0.2 ng g^{-1} to 9.95 μg g^{-1}, with the ng g^{-1} level in most samples. For plant samples, Asami [5] reported Te concentrations ranging from 18 to 33 ng g^{-1} in Japanese plants. Generally, the Te level in plant samples depends on the plant species and the level of Te in the soil or the surrounding environment. Higher concentrations of Te in plants could also be expected in mining areas, for example, in the Ely mining district of White Pine County, NV, USA, plants known to accumulate selenium were found to be able to accumulate Te up to the level of approximately 1 μg g^{-1} [7].

Due to the low concentration of Te in the environment, the determination of Te in soil and plant samples has been a great analytical challenge. Although many analytical techniques, such as instrumental neutron activation analysis (INAA), graphite furnace atomic absorption spectrometry (GFAAS), quartz tube atomic absorption spectrometry (QTAAS), inductively coupled plasma source atomic emission spectrometry (ICP-AES), and hydride generation atomic fluorescence spectrometry (HG-AFS) have been developed for Te determination in environmental samples [6,8–11], in most cases, because of the relatively high detection limits, tedious preconcentration and separation operations are required due to the complicated matrix composition in soil and plant samples. Recently, sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS) has been widely used for trace element analysis in various environmental samples. The SF-ICP-MS is characterized by an extremely high sensitivity, which is ca. 2 orders of magnitude higher than that of typical quadrupole ICP-MS [12].

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Therefore, using SF-ICP-MS, smaller sample size and much simple sample pretreatment procedure could be expected for the determination of trace Te in soil and plant samples which is necessary to build up the Te soil-to-plant transfer factor data-base for Japan.

Our objective of this study was the development of a simple and sensitive analytical method for the direct determination of trace Te in soil and plant samples using SF-ICP-MS. Soil and plant samples were digested with *Aqua regia;* after appropriate dilution to reduce the matrix effect, Te was directly measured without any separation and pre-concentration steps. We considered the selection of suitable Te isotopes for ICP-MS analysis and the estimation of potential polyatomic interferences for trace level Te analysis. The developed method was validated by the analysis of soil/sediment and plant reference materials, and successfully applied to the study of soil-to-plant transfer of Te in the Japanese environment.

2. Experimental

2.1. Reagents and materials

All the reagents were ultra-pure and used without any further purification. HNO_3, HCl, and HF (grade AA-100) were purchased from Tama Chemicals (Kawasaki, Japan). Te standard solution was obtained from Kanto Chemicals (Tokyo, Japan). Rh standard solution and a multi-element standard solution (SPEX-XSTC 331) were purchased from SPEX CertiPrep (Metuchen, NJ). Milli-Q water (Millipore, MA; 18 MΩ cm^{-1}) was used for the preparation of sample and standard solutions. Soil/sediment reference materials, JSd-1 and JSd-3 (Stream sediment, Japan), JLk-1 (Lake sediment, Japan) and JSO-1 (Soil, Japan) were obtained from the Geological Survey of Japan. Plant reference materials, NIST-SRM-1567a (Wheat flour), NIST-SRM-1568a (Rice flour), NIST-SRM-1570a (Spinach leaves), and NIST-SRM-1573a (Tomato leaves) were purchased from the US National Institute of Standards and Technology (NIST). Finally, five sets of soil and crop samples collected in 2002–2004 were studied for the TF of Te in Japanese agricultural environment.

2.2. Sample preparation

2.2.1. Soil *Aqua regia* digestion

Approximately 0.05 g of powdered soil samples and soil/sediment sample were weighed into a Teflon screw-top vessel (30 mL) (Savillex, Eden Prairie, MN). To each sample 12 mL of *Aqua regia* was added. To avoid the loss of Te due to the leakage of chlorides of Te, which have relatively low boiling points ($TeCl_4$, 390 °C; $TeCl_2$, 327 °C), the sealed vessels were then heated on a hot-plate at 140 °C for 48 h. After cooling, the solution inside was evaporated to incipient dryness at 80 °C. The residue was then dissolved by adding 3 mL conc. HNO_3 (68%), and diluted into a final volume of 50 mL with milli-Q water after adding 0.5 mL of 50 ng mL^{-1} Rh as internal standard. Finally, the solution was centrifuged for 20 min at 3000 rpm, and filtrated through a 0.45 μm syringe filter (Minisart® RC15, Sartorius) prior to analysis.

2.2.2. Soil HNO_3–HF digestion

Approximately 0.05 g of powdered soil samples and soil/sediment sample were weighed into a Teflon screw-top vessel (30 mL), and also digested with 4 mL conc. HNO_3 and 4 mL conc. HF. After drying at 80 °C, the residue was re-dissolved into 1.0 mL of conc. HNO_3 (68%), and the mixture was evaporated to dryness. This treatment was repeated twice. This additional treatment expelled HF to avoid corrosion on the interior system of SF-ICP-MS. The residue was then dissolved by adding 3 mL conc. HNO_3 (68%), and diluted into a final volume of 50 mL with milli-Q water after adding 0.5 mL of 50 ng mL^{-1} Rh as internal standard. Finally, the solution was centrifuged for 20 min at 3000 rpm, and filtrated through a 0.45 μm syringe filter (Minisart® RC15, Sartorius) prior to analysis.

2.2.3. Plant *Aqua regia* digestion

Approximately 0.5 g powdered collected plant samples and plant reference materials were weighed into a Teflon screw-top vessel (30 mL) (Savillex), and digested with 12 mL of *Aqua regia*. The digestion was continued overnight at room temperature in order to provide adequate contact between sample and acid to enhance the acid effect [13] and to avoid excessive reaction during the later heating stage. Then the similar procedure for soil samples with *Aqua regia* digestion was performed. Because the plant samples were completely digested with *Aqua regia*, no HNO_3–HF digestion was applied for them in this study.

2.3. SF-ICP-MS measurement

The Te content in collected soil/plant samples and reference materials of soil/sediment and plant was directly analyzed after acid digestion without any separation and preconcentration steps, except for a 1000-fold dilution for soil/sediment samples and a 100-fold dilution for plant samples to reduce the matrix effect. SF-ICP-MS (Thermo Fisher Scientific, Element 2, Bremen, Germany) was performed in the low resolution (LR) mode in order to utilize the maximal instrument sensitivity. A conventional conical concentric nebulizer mounted on a Scott-type double-pass spray chamber was used as sample introduction system, and it was operated at a sample uptake rate of ~0.1 mL min^{-1}. All the measurements were made in the self-aspiration mode to reduce the risk of contamination from the peristaltic pump tubing. Since the RF power of the SF-ICP-MS has a significant influence on Te signal intensity (see Fig. 1S, in Supporting Information), the SF-ICP-MS was optimized on a daily basis using 1 ng mL^{-1} multi element standard and 1 ng mL^{-1} Te standard solutions to provide optimum intensities and peak shapes of the selected Te isotopes. Optimized operation conditions of SF-ICP-MS are summarized in Table 1. External calibration was performed with Te standard solutions (0–1 ng mL^{-1}) spiked with 0.5 ng mL^{-1} internal standard (Rh).

Table 1
Optimized operating conditions and data acquisition settings for SF-ICP-MS.

SF-ICP-MS	Parameters
Instrument settings	
RF power	1025 W (tiny optimization required daily)
Nebulizer	Conical concentric
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter
Torch	Fassel
Cool gas	16 L min^{-1}
Sample gas (nebulizer gas)	0.97–0.99 L min^{-1} Ć(tiny optimization required daily)
Data acquisition settings	
Low resolution ($m/\Delta m=300$)	
Acquisition mode	E-scan (peak jumping)
Monitored isotopes	^{103}Rh, ^{125}Te, and ^{126}Te
No. of scans (runs × passes)	15 × 5
Mass window	10%
Samples per peak	100
Integration type	Average
Total time of sampling	85 s

3. Results and discussion

3.1. Selection of Te isotope for SF-ICP-MS analysis

For Te analysis using ICP-MS, because of its high first ionization potential (9.009 eV) Te has a lower sensitivity compared to sensitivities of other elements having a low first ionization potential. Generally, it is desirable to select Te isotopes with higher abundance for trace level Te analysis. Te has 8 stable isotopes, namely: ^{120}Te (0.09%), ^{122}Te (2.55%), ^{123}Te (0.89%), ^{124}Te (4.74%), ^{125}Te (7.07%), ^{126}Te (18.84%), ^{128}Te (31.74%), and ^{130}Te (34.08%). However, as shown in Table 2, the two Te isotopes with the highest abundance (> 31%), ^{128}Te and ^{130}Te, have serious isobaric interferences from ^{128}Xe (1.92%), ^{130}Xe (4.08%) and ^{130}Ba (0.106%). It has been reported that background signal intensities at *m/z* 128 and 130 caused by the impurities of ^{128}Xe and ^{130}Xe in ultra-pure argon gas are significantly high, seriously deteriorating the determination of nanogram levels of Te using ICP-MS [9]. Our investigation also confirmed the interferences of ^{128}Xe and ^{130}Xe on Te determination. We measured isotope ratios of ^{128}Te/^{125}Te and ^{130}Te/^{125}Te in 4% HNO_3 solution with different Te concentrations of 0, 0.01, 0.1, 0.5, and 1 ng mL^{-1}. Since ^{125}Te is free of Xe-associated interference, the existence of ^{128}Xe and ^{130}Xe interferences could deviate the isotope ratios of ^{128}Te/^{125}Te and ^{130}Te/^{125}Te from the values based on their natural abundance. As shown in Fig. 1, isotope ratios of ^{128}Te/^{125}Te and ^{130}Te/^{125}Te observed in 4% HNO_3 are close to 100, which is ca. 20 times higher than the values expected based on the natural abundance of Te isotopes, indicating serious interferences of ^{128}Xe and ^{130}Xe. Although the extent of interferences decreased with the increase of Te concentration, the Xe interferences can still be observed even at a concentration of 1 ng mL^{-1}. Thus, ^{128}Te and ^{130}Te were excluded for further investigation. For ^{120}Te, ^{122}Te, ^{123}Te and ^{124}Te, as well as their low abundance (0.09–4.74%), they also have isobaric interferences from Sn, Sb and Xe. These six Te isotopes (^{120}Te, ^{122}Te, ^{123}Te, ^{124}Te, ^{128}Te and ^{130}Te) are thus unsuitable for trace level Te analysis by ICP-MS. The two remaining isotopes, ^{125}Te and ^{126}Te have relatively high abundance (7.07% and 18.84%, respectively). In addition, ^{125}Te has no isobaric interference, and the isobaric interference from ^{126}Xe is not significant for ^{126}Te due to the low abundance of ^{126}Xe (0.09%). Therefore, we selected ^{125}Te and ^{126}Te for further study on Te analysis using SF-ICP-MS.

Table 2
Isobaric interferences on Te isotopes in ICP-MS.

Isotopes	Abundance (%)	Interference	Abundance (%)
^{120}Te	0.09	^{120}Sn	32.58
^{122}Te	2.55	^{122}Sn	4.63
^{123}Te	0.89	^{123}Sb	42.79
^{124}Te	4.74	^{124}Sn, ^{124}Xe	5.79, 0.09
^{125}Te	7.07		
^{126}Te	18.84	^{126}Xe	0.09
^{128}Te	31.74	^{128}Xe	1.92
^{130}Te	34.08	^{130}Xe, ^{130}Ba	4.08, 0.106

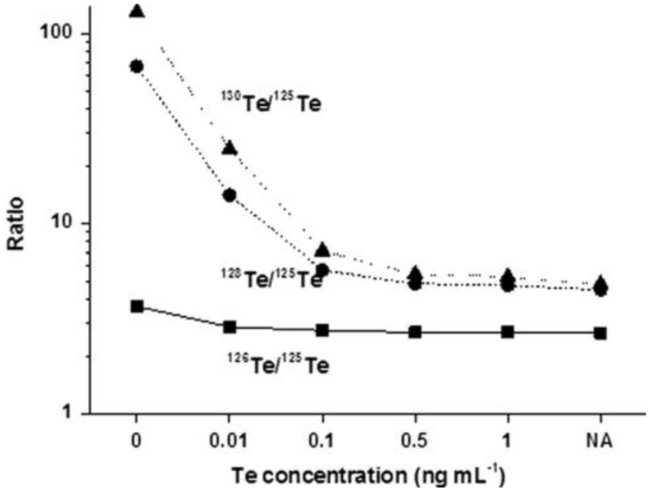

Fig. 1. The influences of Xe on the signal intensities of different Te isotopes in SF-ICP-MS (The Te concentration of 0 ng mL^{-1} represents 4% HNO_3 solution; NA: Natural abundance).

3.2. Instrumental limit of detection for Te analysis

Previous findings indicated that Te concentrations in Japanese soil and plant samples ranged from 10 to 109 ng g^{-1}, and 18 to 33 ng g^{-1}, respectively [5]. In order to reduce the sample matrix effect for direct Te analysis using SF-ICP-MS, a dilution factor of 1000 for soil samples and 100 for plant samples was found to be necessary. This means that limits of detection (LODs) lower than 0.01 ng mL^{-1} for soil samples, and 0.18 ng mL^{-1} for plant samples are required.

Instrumental LOD was estimated using 4% HNO_3 as a blank and a Te standard solution prepared in 4% HNO_3. In order to achieve the best LOD, we compared two sample introduction systems. In our previous studies [14–19], a high efficiency sample introduction system (APEX-Q) was combined with SF-ICP-MS to achieve an extremely low LOD of femtogram level for Pu isotopes, ^{241}Am, ^{99}Tc and Th isotopes analysis in various environmental samples. This system consisted of a heated cyclonic spray chamber, a Peltier cooled condenser and an ACM Nafion fluoropolymer membrane desolvation module. A small flow of nitrogen was used to increase transport efficiency and signal stability. For Te analysis, the APEX-Q/SF-ICP-MS was evaluated under the LR and medium resolution (MR) modes. As shown in Table 3, low LODs, defined as three times the standard deviation (3σ) of the blank sample (4% HNO_3), of 0.00025 and 0.00036 ng mL^{-1} for ^{125}Te and ^{126}Te, respectively, were achieved in the LR mode. In the MR mode, due to the loss of sensitivity by about a factor of 10, one order of magnitude higher LODs of 0.0037 and 0.0013 ng mL^{-1} for ^{125}Te and ^{126}Te were obtained, respectively. For elements with a first ionization potential in the range of 9–11 eV, such as Te (9.009 eV), adding ethanol was reported to be useful to improve the sensitivity due to the carbon charge transfer reaction [20–22]. By adding 3% ethanol to the sample solution, we observed a three-fold sensitivity improvement; however, the background at *m/z* 125 and 126 also increased significantly. Consequently, no improvement of LODs was achieved. Our observation differed from that reported by Hu et al. [9]. Using a quadrupole ICP-MS, they observed a significant LOD improvement

Table 3
Instrument LODs of ^{125}Te and ^{126}Te in 4% HNO_3 from different sample introduction systems of SF-ICP-MS.

Sample introduction systems	Instrument LOD (ng mL^{-1})	
	^{125}Te	^{126}Te
APEX-Q/SF-ICP-MS		
LR	0.00025	0.00036
MR	0.00370	0.00130
LR (3% ethanol)	0.00041	0.00133
Conical concentric nebulizer/SF-ICP-MS		
1.0 mL min^{-1} sample uptake (LR)	0.00031	0.00035
0.1 mL min^{-1} sample uptake (LR)	0.00012	0.00017
MR	0.00322	0.00133

by adding 4% ethanol. The different sample introduction systems which have different responses regarding background level may account for the different results on ethanol addition for LOD improvement.

Better LODs were obtained with a conical concentric nebulizer mounted on a Scott-type double-pass spray chamber as the sample introduction system. With a sample uptake rate of 0.1 mL min^{-1} using the sample uptake tubing with 0.25 mm i.d., we achieved the best LODs of 0.00012 and 0.00017 ng mL^{-1} for ^{125}Te and ^{126}Te, respectively, in the LR mode. As expected, the LODs of ^{125}Te and ^{126}Te increased by factors of 4–10 under the MR mode. We also estimated the LODs under the LR mode by increasing the sample uptake rate to 1.0 mL min^{-1} using a sample uptake tubing with 0.5 mm i.d.; we found that the LODs increased by about a factor of 3 compared to that of the 0.1 mL min^{-1} sample uptake. This deterioration of LODs could be attributed to the drop in fine aerosol forming efficiency during the nebulization, which caused significant loss of uptake samples inside the spray chamber. We noted that all the LODs presented in Table 3 obtained with both the APEX-Q and conical concentric nebulizer mounted on a Scott-type double-pass spray chamber as sample introduction systems were sufficiently low for trace Te analysis in soil (after 1000-fold dilution) and plant (after 100-fold dilution) samples. Considering the better LODs and simplicity of operation, the conical concentric nebulizer with a micro-sample uptake rate of 0.1 mL min^{-1} was selected as the optimized sample introduction system for analysis of soil and plant reference materials and collected samples.

3.3. *Investigation on polyatomic interferences*

Due to the complicated matrix in soil samples, for the direct determination of trace level Te, even after a 1000-fold dilution, the potential polyatomic interferences must be investigated. As summarized in Table 4, the major polyatomic interferences are from the Ar-associated interferences, such as ^{87}Sr^{38}Ar^{+}, ^{87}Rb^{38}Ar^{+}, ^{89}Y^{36}Ar^{+}, and ^{85}Rb^{40}Ar^{+} for ^{125}Te analysis, and ^{88}Sr^{38}Ar^{+}, ^{86}Sr^{40}Ar^{+}, ^{90}Zr^{36}Ar^{+}, and ^{86}Kr^{40}Ar^{+} for ^{126}Te analysis. The *m/z* of these Ar-associated polyatomic interferences is slightly smaller than the *m/z* of ^{125}Te and ^{126}Te; they can be separated from Te isotopes with a mass resolution of ca. 4000, using the MR mode of the SF-ICP-MS. Fig. 2 compares mass spectra under the MR mode with a Te standard solution, a soil reference material sample with *Aqua regia* digestion, and the same soil reference material sample with HNO_3–HF digestion under MR mode. There were obvious polyatomic interferences for ^{125}Te in the soil samples with both *Aqua regia* and HNO_3–HF digestions. ^{126}Te had much less polyatomic interference. This observation indicated that the Ar-associated polyatomic interferences from Sr, Zr and Kr in soils are negligible for ^{126}Te analysis. The ^{87}Rb^{38}Ar^{+} and ^{85}Rb^{40}Ar^{+} polyatomic

Table 4
Major polyatomic interferences on ^{125}Te (*m/z* 124.90444) and ^{126}Te (*m/z* 125.90331) analyses and required resolution to separate them from Te isotopes by SF-ICP-MS.

	Mass	Abundance Ćof former isotope	Abundance Ćof latter Ćisotope	Resolution Ć*m*/△*m*
Potential interferences for ^{125}Te				
^{87}Sr^{38}Ar	124.87162	7.0015	0.0632	3806
^{87}Rb^{38}Ar	124.87191	27.8346	0.0632	3840
^{89}Y^{36}Ar	124.87341	100.0000	0.3365	4025
^{85}Rb^{40}Ar	124.87418	72.1654	99.6003	4128
^{109}Ag^{16}O	124.89966	48.1608	99.7628	26,131
^{107}Ag^{18}O	124.90426	51.8392	0.2000	693,914
Potential interferences for ^{126}Te				
^{88}Sr^{38}Ar	125.86835	82.5845	0.0632	3601
^{86}Sr^{40}Ar	125.86165	9.8566	99.6003	3022
^{90}Zr^{36}Ar	125.87226	51.4520	0.3365	4055
^{86}Kr^{40}Ar	125.87299	17.29835	99.6003	4152
^{109}Ag^{17}O	125.90388	48.1608	0.0372	220,883

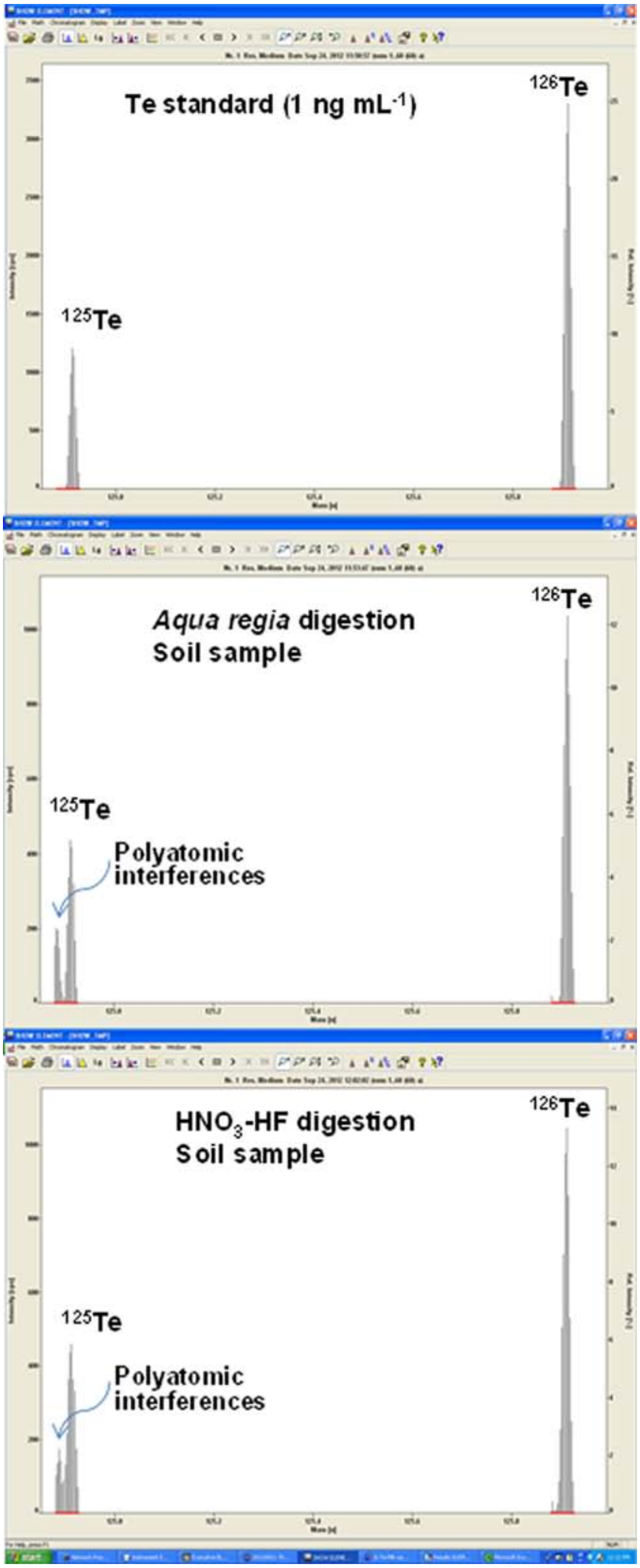

Fig. 2. Mass spectrum obtained under the MR mode for a Te standard solution (1 ng mL^{-1}), soil reference material sample with the *Aqua regia* digestion (dilution factor 1000), and soil reference material sample with HNO_3–HF digestion (dilution factor 1000), respectively. Polyatomic interferences for ^{125}Te analysis were obvious in spectra for both *Aqua regia* and HNO3–HF digestions.

interferences are significant for ^{125}Te analysis due to the high concentration of Rb in soils (12–105 mg kg^{-1} in Japanese soils) [23]. Therefore, for the direct Te analysis in soils, ^{125}Te is not a good choice, although this isotope has been used for the analysis of Te in geological materials [3,8,24].

Another potential polyatomic interference from AgO^+ has to be considered because of the relatively high concentration of Ag in soils (~100 ng g^{-1} in Japanese soils) [25–27]. As shown in Table 4, to separate $^{109}Ag^{16}O^+$ and $^{107}Ag^{18}O^+$ from ^{125}Te, and $^{109}Ag^{17}O^+$ from ^{126}Te, extremely high mass resolution ranging from 26,000 to 693,900 is required, which is not achievable with current mass spectrometers. To estimate this potential interference for Te analysis, we investigated the influence of Ag concentration on signal intensities at *m/z* 125, 126, and 130 under the LR mode. For the determination of soil samples, a 1000-fold dilution was applied, thus the maximum Ag concentration of ~0.1 ng mL^{-1} in the final solution for analysis could be expected. As shown in Fig. 3, there was no significant influence from AgO^+ polyatomic interferences on the signal intensities of ^{125}Te and ^{126}Te using our SF-ICP-MS analytical system, although a slight increase of ^{125}Te signal intensity was observed when the Ag concentration was increased to 0.5 ng mL^{-1}. Therefore, we concluded that for ^{126}Te analysis, the $^{109}Ag^{17}O^+$ polyatomic interference was negligible due to the low abundance of ^{17}O (0.0372%). After a comprehensive investigation on the potential polyatomic interferences, we selected ^{126}Te isotope for Te analysis.

3.4. Validation of analytical method

The developed analytical method was validated by the analysis of reference materials. For soil analysis, three sediment reference materials (JSd-1, JSd-3, and JLk-1) and a soil reference material (JSO-1) were analyzed. The sediment reference materials, JSd-1, JSd-3, and JLk-1, have reference Te concentration values of 21, 264, and 113 ng g^{-1}, respectively. Te concentration in soil reference material, JSO-1 has a certified value of 85 ± 4 ng g^{-1}. Four plant reference materials, NIST-SRM-1567a (wheat flour), NIST-SRM-1568a (rice flour), NIST-SRM-1570a (spinach leaves), and NIST-SRM-1573a (tomato leaves) were analyzed. No certified or information value of Te concentration in these plant reference materials is available.

Fig. 4 presents the analytical results of Te in soil/sediment reference materials using *Aqua regia* and HNO_3–HF digestions. The results obtained from both digestion methods were generally in good agreement with the certified/reference values, especially for the *Aqua regia* digestion, the measured values had a relative difference less than 10% compared to the certified/reference values, indicating the good accuracy of the developed analytical method. The precision of the developed analytical method was estimated by measuring external reproducibility determined by the analysis of three digestions of the reference materials. For soil and sediment reference materials, the relative standard deviation varied from 1.2% to 7.5%. Considering the simplicity of digestion operation for large amounts of samples, the *Aqua regia* digestion method was finally selected for soil and plant analysis for the study of soil-to-plant transfer of Te.

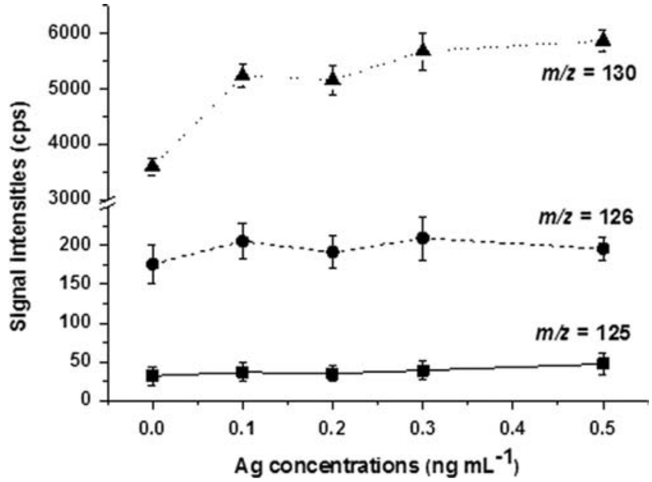

Fig. 3. Effect of AgO+ polyatomic interferences on Te analysis at *m/z* 125, 126 and 130.

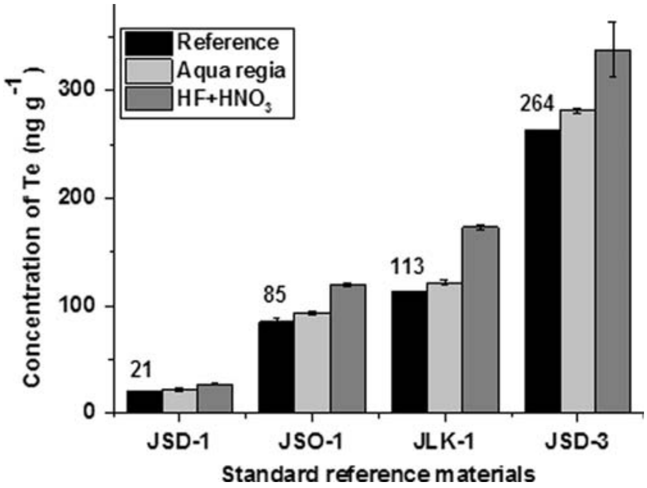

Fig. 4. Analytical results of Te concentrations in soil and sediment reference materials obtained with the *Aqua regia* digestion and HNO_3–HF digestion, respectively.

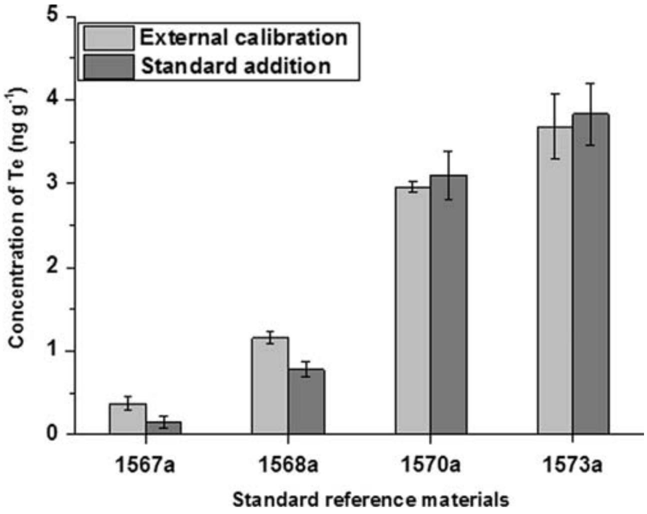

Fig. 5. Comparison of analytical results between the external calibration method and standard addition method for the plant reference materials from NIST.

Since no certified or information values for Te in plant reference materials are available, the four plant reference materials were analyzed by both the external calibration method and standard addition method with the *Aqua regia* digestion. As shown in Fig. 5, the results of these two calculation methods were in good agreement. We also made a recovery test for the digestion of plant samples by adding Te (about 2 times of the determined concentrations of the four plant reference materials), and high recovery ranging from 97% to 107% was obtained, indicating that a simple external calibration method was accurate for Te analysis in plant samples using the *Aqua regia* digestion following a 100-fold

Table 5
Comparison of the different analytical methods and their LODs in recent reports.

Sample	Digestion	Sampling introduction	Measurement	LOD (ng g^{-1})	Note	Ref.
Soil and river sediment	HNO_3–HF–H_3BO_3, microwave	Cross flow nebulizer	quadrupole ICP-MS	Not reported Te isotope unknown	No separation, DF[a] 5000	[13]
Rock	HNO_3–HF–HCl, high pressure digestion	Dual inlet borosilicate glass spry chamber	ID-HG-MC-ICP-MS	$<$ 1 (^{125}Te and ^{126}Te)	Thiol cotton fiber separation	[3]
Silicate rock and soil	HNO_3–HF, high pressure digestion	Microconcentric nebulizer and cyclonic spray chamber	ICP-MS	0.5 (^{126}Te), 0.8 (^{128}Te)	DF 1000	[9]
Basalt rock	HNO_3–HF, high pressure digestion	Porous membrane	ID-HG-ICP-MS	0.003 (^{125}Te and ^{126}Te)	Cation exchange column separation	[8]
Stream sediment and rock	*Aqua regia* or HNO_3–HF–$HClO_4$–HCl	Hydride generation	HG-ICP-MS	1 (^{128}Te and ^{130}Te)	Co-precipitation	[29]
Silicate materials	HF–HNO_3–Br_2	Normal	ID-ORC-ICP-QMS	0.1 (^{125}Te), 0.07 (^{126}Te)	No separation, DF~70	[24]
Geological materials (rock, soil, deposit etc)	*Aqua regia* and HF		Graphite furnace atomic absorption spectrometry	0.2	Solvent extraction	[6]
Stream sediment, coal fly ash and garlic	H_2O_2–HNO_3–HF microwave	Hydride generation-integrated atom trap atomizer	Flame atomic absorption spectrometry	0.9 ng mL^{-1}	2 mL sample uptake	[30]
Soil	*Aqua regia*	Conical concentric nebulizer	SF-ICP-MS	0.17 (^{126}Te)	No separation, DF 1000	This study
Plant				0.02 (^{126}Te)	No separation, DF 100	

[a] DF stands for dilution factor.

Table 6
Te concentrations in Japanese soil and plant samples.

Crop	Soil	Sampling site	Te in crop (ng g^{-1}-dry)	Te in soil (ng g^{-1}-dry)	TF
Potato	Andosol	Hokkaido	0.06 ± 0.01	65.0 ± 3.9	8.7×10^{-4}
Carrot leaf	Cambisol	Mie	3.77 ± 0.32	85.5 ± 8.8	4.4×10^{-2}
Japanese radish leaf	Andosol	Yamaguchi	3.53 ± 0.29	33.4 ± 0.6	1.1×10^{-1}
Japanese radish	Andosol	Yamaguchi	1.23 ± 0.12	33.4 ± 0.6	3.7×10^{-2}
Lettuce	Andosol	Nagano	3.07 ± 0.48	212 ± 4	1.5×10^{-2}
Lettuce	Fluvisol	Kagawa	1.59 ± 0.12	16.2 ± 0.8	9.9×10^{-2}

dilution. The Te concentrations in the four analyzed plant reference materials from US NIST-SRM-1567a (wheat flour), NIST-SRM-1568a (rice flour), NIST-SRM-1570a (spinach leaves), and NIST-SRM-1573a (tomato leaves) were 0.37 ± 0.08, 1.16 ± 0.08, 2.96 ± 0.07, and 3.68 ± 0.39 ng g^{-1}, respectively. The detected Te concentration in NIST-SRM-1568a was in good agreement with the report (1.3 ± 0.4 ng g^{-1}) from Kuo and Jiang [28]. The Te concentrations in the four analyzed plant reference materials from the US ranged from 0.37 to 3.68 ng g^{-1}, which were lower than values found in Japanese plant samples (18–33 ng g^{-1}) [5].

The method LODs, defined as three times the standard deviation (3σ) of the procedure blank sample, were calculated to be 0.17 ng g^{-1} for soil samples and 0.02 ng g^{-1} for plant samples determined with ^{126}Te. Since high purity acids were used for the digestion, and 1000-fold dilution (with 4% HNO_3) was conducted, the procedure blank was found to be same as that of 4% HNO_3 (~80 cps). The LODs obtained in our simple and direct Te analytical method without any complicated separation and preconcentration steps were comparable to or even better than those of most previously published analytical methods which require tedious separation, preconcentration, and determination steps (Table 5).

Recently, coupling hydride generation to ICP-MS for Te measurement has been applied to improve the LOD since Te can form gaseous hydrides at ambient temperature (TeH_2) [3,9,29]. For example, Forrest et al. [8] achieved a very low LOD of 0.003 ng g^{-1} for basalt rock sample using acid digestion, solvent conversion, cation exchange resin separation followed by HG-ICP-MS analysis. However, there are many problems for HG-ICP-MS analysis; for example, oxidation state adjustment is needed for the most reactive state (Te^{IV}) for generation of the hydride species; the introduction of gaseous hydrides may cause problems of plasma stability and memory effect; and interferences from transition metals and hydride-forming elements have been reported [8,9,29]. Furthermore, efforts are needed to treat the boron in waste solutions and attention needs to be paid to the potentially dangerous H_2 and B_2H_6 resulted from $NaBH_4$ [24].

3.5. *Application to the determination of Te in Japanese soil and plant samples*

The developed method was applied to the determination of Te in soil and plant samples collected in 2002–2004 from Kagawa, Nagano, Yamaguchi, Mie and Hokkaido Prefectures. Table 6 summarizes the concentrations of Te in soil and plant samples, and the calculated TF. Concentrations of Te in soil and plant samples ranged from 16.2 to 212 ng g^{-1}, and 0.06 to 3.77 ng g^{-1}, respectively. The Te concentrations in soil samples were comparable with those previously reported by Asami (10–109 ng g^{-1}) [5], while Te concentrations in plant samples were much lower than those reported (18–33 ng g^{-1}) in Japanese plants and American trees, flowering plants and cactuses (6–100 ng g^{-1}) [5,7].

The TF is defined as the uptake of elements by plants from the soil, and calculated by dividing Te concentration in a plant (ng g^{-1}) with that in the soil (ng g^{-1}) [31,32]. The lack of Te concentration data in soil and plant samples resulted in only five temperate environmental TF values of Te being reported in IAEA-TRS-472 [2]. Until now, there had been no TF data on Te available for samples collected in Japan. We have obtained the first TF values on Te in this study from 5 sets of Japanese soil and plant samples and the values ranged from 8.7×10^{-4} to 1.1×10^{-1}, which were relatively low compared to the values (0.1–1.0) reported in IAEA-TRS-472 [2]. Future efforts should be directed toward the study of Te distributions in Japanese agriculture and to build-up the TF database of Te in Japan.

4. Conclusion

A sensitive and simple analytical method for the determination of Te in soil and plant samples was developed using SF-ICP-MS. The Te content in soil and plant samples was directly analyzed after acid digestion and appropriate dilution without further sample manipulation such as ion exchange chromatographic separation and complicated hydride generation analysis. The developed analytical method was validated by the analysis of Te in soil/sediment and plant reference materials. High sensitivity and sufficiently low detection limits of 0.17 ng g^{-1} for soil and 0.02 ng g^{-1} for plant samples were achieved. The satisfactory detection limits and the simple sample preparation make the developed analytical method extremely useful for the determination of trace level Te in Japanese soil and plant samples. That will allow a database of Te TF in Japanese samples to be built up for the study of radioactive Te-induced internal radiation dose, in emergencies, like the Fukushima DNPP accident.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.05.015.

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