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.

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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; $18\ M\Omega\ cm^{-1}$) 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