

Direct determination of tellurium in soil and plant samples by sector-field ICP-MS for the study of soil-plant transfer of radioactive tellurium subsequent to the Fukushima Daiichi Nuclear Power Plant accident

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The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused the release of large amounts of radioactive Te into the environment. Stable Te, as an analogue, is considered to be useful for the estimation of the soil-plant transfer of radioactive Te. It is necessary to estimate the radiation dose of Te that would result from food ingestion. However, due to the extremely low concentrations of Te in the environment, reported transfer factor values for Te are considerably limited. We report a sensitive analytical method for direct determination of trace Te in soil and plant samples using a sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS). The developed analytical method is characterized by a very low detection limit at the sub-parts per billion (ng g^{-1}) level in soil and plant samples, and it has been applied to the study of soil-plant transfer to collect transfer factor data in Japan.

Key Words : FDNPP, Tellurium; ICP-MS; Soil contamination; Transfer factor,

1. Introduction

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused the discharge of large amounts of radionuclides, which included Te-127m ($T_{1/2}=109$ d), Te-129m ($T_{1/2}=33.6$ d), Te-131m ($T_{1/2}=30$ h), and Te-132 ($T_{1/2}=3.204$ d), into the environment¹. Although most of the released Te isotopes had short half-lives, it was suspected that internal doses resulting from the inhalation of these radionuclides would be detected. It is also necessary to consider the relatively long-lived radionuclides among the released Te isotopes, such as Te-127m because it is a beta emitter. This radioactive Te isotope may have increased the internal radiation dose via crop uptake, since it is found that more than 90% of the fission products from the FDNPP accident remained in the soil samples².

However, internal radiation dose estimation was

difficult because of the lack of environmental transfer data for Te. Stable Te, which can be an analogue of radioactive Te isotopes, is useful and important for the estimation of the soil-plant transfer factor (TF) of radioactive Te. Unfortunately, due to the extremely low concentrations of Te in the environment, for example, 10–109 ng g^{-1} in soil and 18–33 ng g^{-1} in plants in Japan³, there are no reported TF values for Te, and only a small amount of data was available internationally⁴.

The determination of Te in soil and plants has been a great analytical challenge due to the absence of sufficiently sensitive and robust analytical methods⁵. Although many analytical techniques have been developed for Te determination in environmental samples, in most cases, a relatively high detection limit and tedious preconcentration and separation operations are inevitable^{6, 7}. These drawbacks make them unsuitable for the determination of trace Te in soil and plant samples, which

is required for the precise study of soil-plant transfer.

In this work, we propose a sensitive and high sample throughput analytical method for the direct determination of trace Te in soil and plant samples using a sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS) with a conventional sample introduction system. The developed analytical method is characterized by a very low detection limit at the sub-parts per billion (ng g^{-1}) level in soil and plant samples, and it has been used for the estimation of soil-plant transfer in Japan.

2. Experimental methods

(1) SF-ICP-MS

A SF-ICP-MS (Element 2, Bremen, Germany) was used in this study. All measurements were performed in the self-aspirating mode to reduce the risk of contamination from the peristaltic pump tubing. To determine Te at trace level using ICP-MS, considerable interference is produced by the xenon in ultrapure argon gas, which hampers the use of high abundance isotopes, for example, ^{128}Te (31.69%) and ^{130}Te (33.80%), because of the high abundance of ^{128}Xe (1.92 %) and ^{130}Xe (4.08%). Therefore, in this work, we selected ^{125}Te (7.14% in abundance) and ^{126}Te (18.84% in abundance) for Te analysis. The SF-ICP-MS was optimized on a daily basis using 1 ng mL^{-1} multi element standard (Merck standard) and 1 ng mL^{-1} Te standard solutions. External calibration was performed using Te standard solutions spiked with the internal standard (Rh).

(2) Chemical and reagents

All the reagents used were of ultrapure degree without any further purification. HNO_3 , HCl , HF , and H_2O_2 (grade AA-100) were purchased from Tama Chemicals (Japan). Te standard solution was obtained from Kanto Chemicals (Tokyo, Japan) and Rh standard solution from SPEX CertiPrep (internal standard). Milli-Q water (Millipore, MA) was used for the preparation of sample solutions.

The following reference materials were analyzed: JSd-1 and JSd-3 (Stream sediment, Japan), JLK-1 (Lake sediment, Japan), JSO-1 (Soil, Japan), NIST-1567a (Wheat flour), NIST-1568a (Rice flour), NIST-1570a (Spinach leaves), and NIST-1573a (Tomato leaves).

(3) Sample decomposition

Approximately 0.05 g of the powdered soil/sediment sample or 0.5 g of the powdered plant sample was weighed into a PTFE pressure vessel. To each sample was added 12 mL of *aqua regia*. The vessels were capped and allowed to stand overnight at room temperature. The sealed vessels were then heated on a hot-plate to 140°C for 48 h. After cooling, the solution inside was evaporated to incipient dryness at 80°C . Then, 1.0 mL of conc. HNO_3 (68%) was added to the solution and the mixture was evaporated to dryness. This treatment was performed twice. For the plant samples, H_2O_2 was added until complete digestion was achieved. The residue was

dissolved using 3 mL conc. HNO_3 and then diluted to a volume of 50 mL with milli-Q water. Rh internal standard solution (0.5 mL of 50 ng mL^{-1}) was added during the procedure of dilution. Finally, the solution was centrifuged for 20 min at 3000 r min^{-1} , and the supernatant was filtrated through a $0.45 \mu\text{m}$ syringe filter prior to analysis.

For comparison, soil/sediment reference materials were digested using the HNO_3 -HF method. An approximately 0.05 g powdered soil/sediment sample was weighed into a new PTFE pressure vessel. To each sample was added 4 mL of conc. HNO_3 and 4 mL conc. HF (48%). After the digestion, a procedure similar to *aqua regia* digestion was performed.

After a series of optimizations on SF-ICP-MS measurement, Te was determined by applying a conventional pneumatic concentric nebulizer mounted on a Scott-type double-pass spray chamber with a sample uptake rate of $\sim 0.1 \text{ mL min}^{-1}$. To obtain a high sensitivity of SF-ICP-MS, Te was analyzed in a low resolution (LR) mode. The optimized instrument conditions used for the determination of Te isotopes are summarized in Table 1. The Te content in soil/sediment and plant samples was directly analyzed after acid digestion without any separation and preconcentration, except for the use of a 1000-fold dilution for soil/sediment samples and a 100-fold dilution for plant samples to reduce the matrix effect.

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

RF power	1025 W
Nebulizer	Conical concentric
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, X-cone
Spray chamber	Scott-type
Sample uptake rate	0.1 mL min^{-1}
Resolution	Low ($m/\Delta m=300$)
Acquisition mode	E-scan (peak jumping)
Monitored isotopes	^{103}Rh , ^{125}Te and ^{126}Te
No. of scans (runs \times passes)	15×5
Mass window	10%
Samples per peak	100
Total time of analysis	85 s
Integration type	Average

3. Results and discussion

(1) Detection limits

The detection limits, defined as three times the standard deviation (3σ) of the process blank sample, were calculated to be 0.17 ng g^{-1} for soil and sediment samples and 0.02 ng g^{-1} for plant samples for ^{126}Te . These values of the detection limits, obtained without the need for any

complicated separation and preconcentration steps, were comparable with or even better than the previously published detection limits estimated using tedious separation, preconcentration, and determination steps^{8,9}.

(2) Accuracy and precision

The accuracy of the developed method was evaluated by a comparison of the analytical data obtained for the aforementioned soil and sediment reference materials with their certified or information values (21–264 ng g⁻¹).

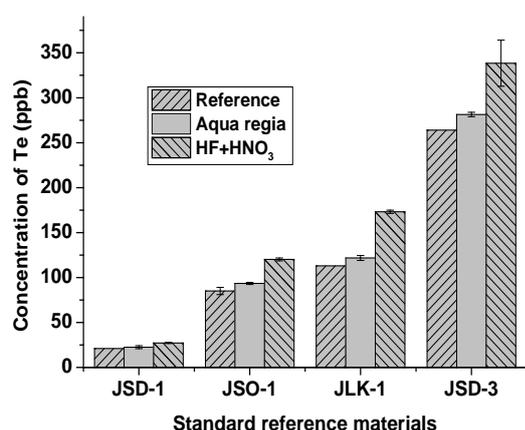


Figure 1. Analytical results of Te concentrations in soil and sediment reference materials obtained with *aqua regia* digestion and HNO₃-HF digestion.

As shown in Figure 1, the analytical results determined with ¹²⁶Te using *aqua regia* digestion were in good agreement with the certified or information values (with the relative deviations of 6.7–10.0%). Interestingly, the relative deviations were somewhat high, ca. 28.2–53.2%, in the case of HNO₃-HF digestion. Furthermore, the results in the case of HNO₃-HF digestion were higher than the certified or information values, possibly due to polyatomic interferences at m/z = 126. Therefore, *aqua regia* digestion was selected as the preferred method in the present work.

The precision of this method was assessed by measuring external reproducibility which was determined by analysis from three digestions of the reference materials. For soil and sediment reference materials, the relative standard deviation varied from 1.2% to 7.5%.

(3) Estimation of potential soil-to-plant transfer factor

The soil-to-plant transfer factor (TF) of Te is the uptake of Te by plants from soil, which is defined as the concentration in the plant sample (ng g⁻¹ dry weight) divided by the concentration in soil (ng g⁻¹ dry weight). Technical reports series No. 472 of IAEA (IAEA-TRS-472) has presented some TFs for Te in a temperate environment (Table 2)⁴. However, the present data on Te are scarce and limited to specific areas and plant species. Furthermore, no other data have been

collected in Japan and other Asian countries.

Table 2. Temperate environmental soil-to-plant transfer factors of Te reported by IAEA-TRS-472⁴.

Plant compartment	N	TFs
Grain	1	1.0×10 ⁻¹
Leaves	1	3.0×10 ⁻¹
Fruits, heads, berries, buds	1	3.0×10 ⁻¹
Roots	1	3.0×10 ⁻¹
Tubers	1	2.0×10 ⁻¹
Stems and shoots	1	1.0

The determined results (0.2–2.4 ng g⁻¹ dry weight) of plant standard reference materials from the National Institute of Standards and Technology (NIST) are presented in Figure 2. Asami *et al.* reported a relatively high mean Te concentration (24 ng g⁻¹ dry weight) in Japanese plant samples, as compared to the determined values reported by us³. Since the samples used by Asami *et al.* were collected from only three sites in Japan, their values may not be representative of the concentration range in Japanese agricultural plants.

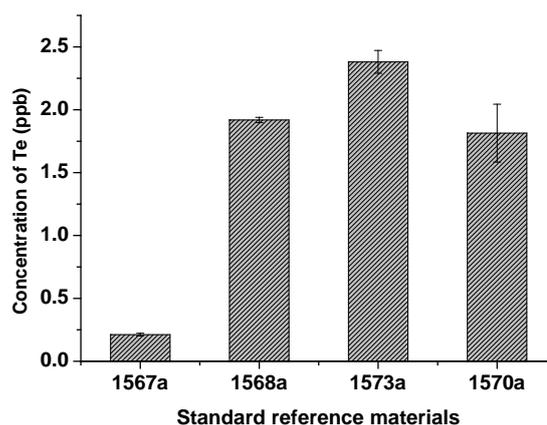


Figure 2. Tellurium concentrations in plant standard reference materials of NIST.

Therefore, we hypothesized that the relatively low concentrations from the American plant (ca. 2 ng g⁻¹) form the lower limit among plants, in order to roughly estimate the TFs of Te in Japan for the Te concentration range of 10–109 ng g⁻¹ in Japanese soils³. The estimated TFs of the likely amount of Te in the environment in Japan ranged from 0.02 to 2, which are comparable with those published in the IAEA-TRS-472 (0.10–1.0)⁴. The TFs of Te that are published in the IAEA-TRS-472 are not sufficient to make a strong, credible comparison. This also confirms the urgent need to collect TF data in order to build a data base for Japan, which would be required for the study of soil-plant transfer of radioactive Te resulting from the soil contamination that occurred due to the nuclear accident.

By using the estimated TF of Te, we could estimate the

daily effective dose resulting from the consumption of food prepared using plants collected from highly contaminated areas by using the following equation:

$$\text{Daily dose (mSv day}^{-1}\text{)} = C_{\text{soil}} \times \text{TF} \times m_{\text{food}} \times \text{CF}$$

where C_{soil} (kBq kg⁻¹) is the ^{129m}Te concentration in soil samples collected at 11 locations outside the 20-km exclusion zone¹⁰⁾; TF is the estimated TFs of Te in the present study (0.02–2.0); m_{food} (kg day⁻¹) is the mass of food consumed on a daily basis by people aged 15 to 19¹¹⁾; and CF (mSv kBq⁻¹) is the ingestion dose conversion factor for radionuclides given by the IAEA-TECDOC-1162¹²⁾. The age group of 15–19 was selected because their agricultural crop consumption was the highest among the other age groups. We set calculation conditions as follows:

(1) The average daily food consumption in 2010 was 548.7 g of cereal, 53.5 g of tubers, 41.8 g of beans, and 232.8 g of green vegetables (cooked); Japanese people consume substantial amounts of white rice, and the weight ratio of cooked to raw rice is 2.3; therefore, cereal data were equivalently considered as 238 g of raw rice. Thus, the total weight of crops used daily for preparing food was estimated to be 567 g.

(2) According to Yamamoto et al.¹⁰⁾, the geometric mean ^{129m}Te concentration in soil collected from outside the 20-km exclusion zone at an air dose rate within 14 μSv h⁻¹ (on March 27–28, 2011) was 1260 Bq kg⁻¹ (corrected to March 11, 2011).

(3) Half of the crops were obtained from the noncontaminated areas.

The roughly estimated daily effective dose due to ingestion of crops, calculated one year after the earthquake, was 1.7×10^{-5} to 1.7×10^{-3} μSv for ^{129m}Te. Assuming that the ^{127m}Te concentration was one-third that of ^{129m}Te¹⁾, the daily dose from intake of ^{127m}Te was 8.2×10^{-4} to 8.2×10^{-2} μSv. A new regulation value for the permitted annual dose due to ingestion of contaminated food has been set to be below 1 mSv in Japan¹³⁾, thus, 2.74 μSv d⁻¹ is the upper limit of the daily dose; obviously, the estimated total dose of ^{129m}Te and ^{127m}Te due to ingestion was about 30 times lower even when the highest TF = 2 was used.

4. Conclusion

A rapid and simple analytical method for the determination of Te in soil and plant samples was developed by using SF-ICP-MS. The Te content in soil and plant samples was directly analyzed after acid digestion and appropriate dilution. The analytical results determined with ¹²⁶Te using *aqua regia* digestion were in good agreement with the certified or information values of reference materials. The excellent detection limits of 0.17 ng g⁻¹ for soil and 0.02 ng g⁻¹ for plant made it possible to estimate the soil-to-plant transfer factor in Japanese environment.

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