Low-level Technetium-99 Determination in Soil Samples by ICP-MS

Shigeo UCHIDA* and Keiko TAGAMI

Address: Environ. & Toxicol. Sci. Res. Group, National Institute of Radiological Sciences, Anagawa 4-9-1, Inage-ku, Chiba-shi, Chiba, 263-8555, JAPAN, *E-mail: s_uchida@nirs.go.jp

A simple separation method was developed for ⁹⁹Tc in soil samples as follows. After incineration, Tc in a soil sample was volatilized in a combustion apparatus for 3 h at 1000°C and trapped in deionized water. The trap solution was passed through an extraction chromatographic resin (TEVA resin, Eichrom Ind. Inc.) and the resin was washed with 2M HNO₃. Technetium was eluted with 5mL of 8M HNO₃ and this fraction was evaporated to dryness at <70°C. The residue was dissolved in 5mL of 2% HNO₃ solution and the ⁹⁹Tc concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS). The numbers of separation steps were less than those of acid leaching methods and the recoveries were usually higher than 60%. However, for the case of a carbonate rich soil sample, the recovery decreased remarkably because the sample matrix fixed Tc in itself during the volatilization step. The ⁹⁹Tc concentrations in Japanese soils were measured in samples prepared using the method and values ranged from 0.004 - 0.11 Bq/kg.

INTRODUCTION

Technetium-99 is of great practical importance because it is one of the fission products with a relatively high yield in the thermal neutron fission of ²³⁵U or ²³⁹Pu (ca. 6%) and it has a long half-life of 2.1 x 10⁵ y. At present, the ⁹⁹Tc from nuclear weapons testing in the atmosphere (1945 - 1963) is the main source of the nuclide in the terrestrial environment. In the future, the quantity of ⁹⁹Tc in the environment may increase due to releases from uranium enrichment facilities, reprocessing plants or nuclear fuel waste disposal vaults. For these reasons, ⁹⁹Tc deserves special consideration in environmental dose assessment to humans and analysis data of ⁹⁹Tc in soil samples should give useful information for predicting the nuclide behavior. However, the ⁹⁹Tc must be separated and concentrated prior to determination because of its low concentration.

An extraction step for ⁹⁹Tc from soil samples has commonly been carried out with acid reagents during heating before measurements are made.¹⁴ Most of the nuclide can be dissolved by this procedure, but other elements in the soil are also dissolved and they interfere with the chemical purification of Tc. When the amount of soil is less than 10 g, the acid leaching technique is attractive because several samples can be handled at once. However, for non-contaminated soils, a lager sample amount (e.g., >100g) is usually necessary for the ⁹⁹Tc determination; if the acid leaching method is applied, large amounts of acid reagents are necessary and the following chemical separation steps are complicated. Consequently, the chemical recoveries are variable. To simplify and provide high recovery from a large amount of soil samples, we had proposed a separation method using a combustion apparatus.^{5,6} In the present study, we have summarized the results of the combustion apparatus applications for ⁹⁹Tc separation from several soil samples. We have checked whether the method can be used for all types of soil samples or not.

EXPERIMENTAL Apparatus The combustion apparatus consists of two electric tube ovens (300 - 1100°C), a temperature regulator, a driving unit for the ovens, a couple of quartz combustion tubes, two gas flow meters for the tubes, and two vertical traps which include aqueous solution.

The ICP-MS used was the Yokogawa model, PMS-2000. For low-level ⁹⁹Tc measurement of sample solution, the counting time was set to 180 s at mass 99. To check levels of potential interference elements (e.g., Ru, Mo), m/z = 98, 101 and 102 were also scanned at the same time. The detection limit of ICP-MS was 0.03 mBq/mL.



Fig. 1. Loss of ^{95m}Tc from soil samples as a function of heating time when incinerated at 450ûC. Freshly contaminated soil (■); 1 month contaminated Andosol (○); 1 month contaminated Gray lowland soil (○); 6 month contaminated soil (● Bars indicate counting errors.

Technetium volatilization behavior during heating in a combustion apparatus

A soil classified as Andosol was used. The soil had been contaminated with ⁹⁹Tc for 1 y. The sample soil was incinerated at 450°C for 8 h. Then, it was mixed with ^{95m}Tc 3 h before the test. The sample was heated in the combustion apparatus from 500 to 1000°C. The temperature was raised to the next step in a 100°C increments during a 10 min period and held there for 50 min. Oxygen gas was passed through the tube during heating. The volatilization at 1000°C was carried out twice for each sample.

To trap the volatilized Tc, it would be better to use an alkaline solution or a solution with an oxidizer because of the chemical stability of Tc in these solutions. We also have found that deionized water could trap Tc as well as the alkaline solution did.⁶ When deionized water was used, it was easier to adjust the acidity of this trap solution to approximately 0.1M HNO₃ for TEVA resin extraction. Thus, deionized water was used as trap solution. The trap solutions, each 150 mL, were changed at the end of each step. 100 mL of a trap solution were transferred into a plastic vessel (250 mL) and the activity of ^{95m}Tc in the solution was measured with a Ge detector system (Seiko EG&G). Tc-99 was measured by ICP-MS.

Measurement of global-fallout ⁹⁹Tc in surface soils

All the soil samples were air-dried and passed through a 2 mm mesh sieve and incinerated at 450°C for 8 h. Then, about 50 g of soil sample were placed in an inner tube of the combustion apparatus and the ovens were heated at 1000°C for 3 hours. During heating, Tc was evaporated from the sample and was collected in two vertical traps, each containing 150mL of deionized water. After heating was completed, this sample was replaced with another 50 g batch of the same incinerated soil sample and the combustion procedure was repeated until the accumulated weight of incinerated soil samples was 200 to 300 g. Tc-95m was used as a chemical tracer.

These trap solutions were transferred into a beaker and several drops of H_2O_2 were added to adjust all Tc to TcO₄⁻. The solution was heated on a hot plate at 90°C for 3-4 hours then adjusted to 0.1M HNO₃ with conc. HNO₃. The solution was passed through a TEVA resin column. Because ICP-MS cannot

differentiate between ⁹⁹Ru and ⁹⁹Tc, it is necessary to separate all Ru from the final sample solution prior to ICP-MS measurement. Ruthenium present in the sample solution was not effectively retained on the TEVA resin. More than 95% of the Ru passed directly through the column with the solution. The column was then washed with 40mL of 2M HNO₃ to remove any remaining trace Ru. Technetium was eluted with 5mL of 8M HNO₃. The separation steps completely removed Ru; only <0.1% of the element was found in the 8M HNO₃ eluate. The strip solution containing Tc was evaporated to dryness at <70°C, and the residue dissolved in 5mL of 2% HNO₃.

RESULTS AND DISCUSSION

Soil pretreatment

Soil incineration is usually performed to decompose soil organic matter that interferes with Tc chemical analysis. To clarify the Tc loss during incineration, we measured the loss ratios from aged and freshly contaminated soil samples during incineration. Long-contaminated soil samples (Andosol and Gray lowland soil) were contaminated with ^{95m}Tc for 1 or 6 months. Freshly contaminated soil samples were prepared 1-2 days before the test. Figure 1 shows loss of ^{95m}Tc by incineration as percentage of initial activity. The weight reductions of the Andosol sample and the Gray lowland soil sample were 19 - 25% and 9%, respectively. Despite a difference in organic matter content, there was no loss of Tc in either 1-month contaminated soils during incineration. The results were the same as for 6-month contaminated soil. Loss of ^{95m}Tc gradually increased in freshly contaminated soil by incineration whereas the soil samples contaminated more than 1 month by ^{95m}Tc showed no increase.⁷ This result suggested that most soil samples could be incinerated without any loss of fallout Tc. Thus the soil samples were incinerated at 450°C for 8 hours. However, the loss must be considered when adding Tc freshly to soil samples as a yield monitor.

Technetium volatility behavior during heating

The percentages of ⁹⁹Tc and ^{95m}Tc volatilized from the soil were almost the same (data not shown);

these Tc isotopes showed the same volatility behavior although their contamination periods differed.⁶ Therefore, the freshly added ^{95m}Tc could be used as a yield monitor of originally included ⁹⁹Tc.

The volatility of ^{95m}Tc from the Andosol soil sample is shown in Fig. 2. The ^{95m}Tc volatility increased with temperature. However, second heating at 1000°C showed no remarkable increase of Tc volatilization. It was suggested that Tc in the soil sample was not be completely volatilized even if the temperature of 1000°C was maintained for a longer time. Probably, the Tc volatility was affected by the soil volume, soil components, *etc.* Although Tc volatility did not reach to 100%, the method could separate Tc from soil matrices. Consequently, the following separation steps can be simplified.





Fig.2 Temperature effect on Tc volatilization from an Andosol sample^a.

Place	Year	Range (Bq/kg)	Reference
Japan (paddy field)	1991-1992	0.006-0.11	Tagami and Uchida, 1997 ¹⁰ , 2001 ¹¹
Japan (other)	1991-1992	0.004 - 0.020	Tagami and Uchida, 2001 ¹¹
Germany (forest)	-	0.02 - 0.07	This work
Marshall Islands*	1992-1996	0.10-1.11	Tagami and Uchida, 2000 ¹²
Chernobyl (forest)	1991-1992	1.1 – 13.4	Uchida and Tagami, 1999 ⁹

Table 1. Technetium-99 concentration in surface soil samples.

*Separated by both acid leaching and combustion apparatus methods.

Chemical yield

The total chemical recoveries of Tc by the method are shown in Fig. 3. The use of a combustion apparatus offers significant advantages over acid dissolution techniques for other soil types/elements; the percentages of volatilized Tc were almost constant and the matrix elements contents in the trap solution were notably lower than those of the acid dissolution method. The ranges of element concentrations in the final Tc column eluted solutions were compared using acid leaching and volatilization methods (data not shown). When acid leaching without soil incineration was carried out, some element concentrations were higher than those in solutions obtained from incinerated soil samples. We therefore suggest that careful attention should be given to the type of extraction procedure used, and to the preparation of the sample load solution used for the separation of ⁹⁹Tc on TEVA columns.

Yields of 7.6 - 16.9% were found when Marshall Islands soils were analyzed. The low recoveries appeared to show that Tc was not efficiently volatilized from these soils. Since their main matrix is carbonate, the melted carbonate interfered with the Tc volatility during heating at 1000°C. Therefore, the method cannot be applied to the high carbonate content samples.

Determination of ⁹⁹Tc in environmental soil samples

As described above, the use of the combustion apparatus for Tc separation from large soil samples provides a final cumulative sample which gives satisfactory results in ICP-MS determination. Results are shown in Table 1 when the method was applied to prepare environmental soil samples for ⁹⁹Tc determination. For Japanese soil samples, global fallout ⁹⁹Tc was the main source. The concentration was usually on the order of mBg/kg. Interestingly, the levels in paddy field soils were slightly higher than other soil types collected in Japan. This can be explained by low redox potential conditions when the paddies are flooded for rice plant cultivation.⁸ Technetium might be fixed in the paddy field soil because of the chemical form change due to reduction. When Tc is transformed to a reduced form, the solubility is lower than that of TcO_4 . The contents in the soils collected in Germany are almost the same level as



Fig. 3. Radiochemical recoveries of Tc in soil samples separated by combustion apparatus.

those of the Japanese one. The place where the former were collected is known to have been affected by Chernobyl fallout; because the release of the ⁹⁹Tc was one order of magnitude lower than ¹³⁷Cs that of and most of the ⁹⁹Tc was deposited near the Chernobyl site,⁹ the ⁹⁹Tc addition to the soil by the accident was not remarkable.

These results give us an idea how Tc behaves in the environment, however, the data are still limited. Further studies are needed to obtain the definitive behavior of Tc in the environment.

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