

Study on Determination of Technetium -99 in Environmental Samples

Shing-Fa Fang¹ and Tieh-Chi Chu²

¹Division of Health Physics, Institute of Nuclear Energy Research,
1000 Wen-Hua Road, Chiaan Village, Lungtan, Taoyuan, Taiwan 325

²Institute of Nuclear Science, National Tsing Hua University,
Hsinchu, Taiwan 300

Introduction

Technetium, with atomic number 43, means artificial derived from Greek. There is no stable technetium isotope exists in the natural world. The first claim to its discovery was in 1908, by M. Ogawa a Japanese scientist. There are 21 technetium isotopes have been known. Among these isotopes, technetium-97 ($T_{1/2}=2.6\times 10^6$ y), technetium-98 ($T_{1/2}=4.2\times 10^6$ y) and technetium-99 ($T_{1/2}=2.13\times 10^5$ y) have longer half-life. The yield of technetium-99 produced by slow neutron induced fission of Uranium-235 and Plutonium-239 is about 6%. The main sources of Technetium-99 in environment are nuclear weapons testing and nuclear fuel reprocessing. It had been recognized as one of important radionuclides in medium and high-level waste for the calculation of long-term collective dose. Therefore analysis of technetium-99 in environmental samples is necessary to assessment of its environment impact. The most stable chemical states of technetium in aqueous solutions are Tc^{+7} (TcO_4^-) and Tc^{+5} (such as TcO_2^+ , $TcO(OH)_2^+$) which depend on pH value and Eh value(1).

The instrument used to measure Tc-99 concentration in a variety of samples can be divided into two major categories, radioactive analysis and non-radioactive analysis. Among the radioactive analysis instruments, both anti coincidence shielded gas flow counting and liquid scintillation counting have a detection limit of 1 mBq. Inductively coupled plasma- mass spectroscopy with a detection limit of 0.02Bq is the most sensitive instrument. All of environmental samples should be pretreated for separation and purification of technetium before being measured by instruments. 3M EmporeTM Technetium Rad Disks had been developed for analysis of technetium in environmental water samples. It contains high-density GD-1 absorbent grains to separate TcO_4^- ion form sample solutions. It has very good absorption ability of TcO_4^- ion when the pH value of solutions is between 2 and 12 with a flow rate below 50 ml/min. However the particulate in sample solutions should be filtrated before using Technetium Rad Disks. Four kinds of environmental water sample come from the area close to Institute of Nuclear Energy Research (INER) are interested in this study. The pretreatment methods of soil sample and vegetation sample to couple with using Technetium Rad Disks also were developed in this study(2, 3, 4).

Experimental

Environmental samples and their pretreatment

Environmental water samples were taken from the area close to INER including shihmen dam water, ditch water, deep well underground water and drinking water. The soil sample is taken from Tainan. The vegetation sample is a kind of tea and taken from shihbon mountain. All of the places mentioned above are in Taiwan. Water samples were added with 2 ml of H_2O_2 solution (Merck GR) while sampling, to keep Technetium in the chemical state of TcO_4^- ion. Water samples were filtrated by whatman 542 filter to eliminate particulate. Then the aqueous sample could be poured to Technetium Rad Disks and the technetium was kept on the disk.

Soil and vegetation samples were incinerated for 8 hours at 400-450°C to decompose organic matter. 100g of soil were dissolved by hydrogen chloride acid (100 ml of Merck 37% GR) and water (100ml) and heated on hotplate. A few ml of H_2O_2 was also added here. After boiling over 30 minutes, the solution was filtered out residues. Then poured the filtrate into 250ml beaker. Added 1 ml ferric ion solution (20 mg Fe^{+3} /ml, made by Iron (III) chloride hexahydrate, Merck GR), 2ml H_2O_2 and 50 ml NH_3 (Merck 25%) into the filtrate. The alkaline mixture was warmed on a hot plate for above 30 minutes to coagulate the hydroxide precipitate. When it is cool down, filter out the precipitate. The filtrate was heated for another 30 minutes, then leave it over-night. The filtrate was filtered by whatman 542 filter to eliminate fine particulate. Then the sample was treated by Technetium Rad Disk to keep the technetium on the disk.

The disk may be dried and placed into a planchet for direct counting in a low background gas proportional counter or placed into a scintillation vial was added 16 ml scintillator (Parkard Insta-Gel) for counting with a liquid scintillation counter (Parkard 2260XL).

Tracer

Stable rhenium was used as a tracer in many studies. It is cheap and readily available. To use stable rhenium replaces of technetium radioisotopes as a tracer can avoid radiological contamination. That is most attractive reason to us. The concentration of rhenium tracer is 1mg/g (Merck ICP standard). It was added into sample solution and measured by inductively coupled plasma mass spectrometry to monitor its recovery of pre-treatment. Technetium-99 was spiked in the sample solution before passing through the disk to monitor the efficiency of technetium rad disk and compared to rhenium.

All of experiment procedures are described in figure 1.

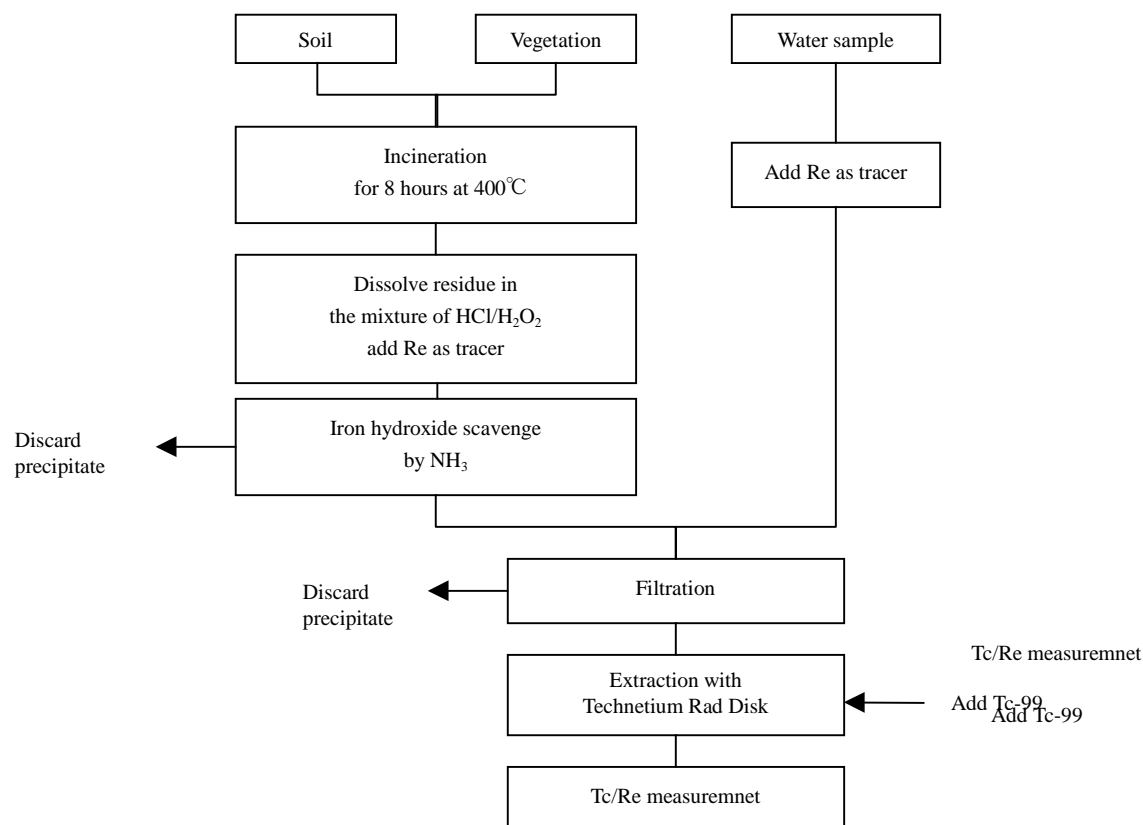


Figure 1. The analytical scheme for separating technetium from environmental materials

Results and Discussions

The efficiency of technetium rad disks do not to be interfered by most of ions, even the chloride ion is above 100000ppm. But when nitric ion concentration is above 2000 ppm will cause interference. Therefore HCl and H₂O₂ are used to dissolve environmental solid sample such as soils and vegetations. There are some organic matters contained in soil and vegetation samples. They should be incinerated with high temperature before dissolution with acids to avoid producing excessive foam and interference. The incineration temperature of oven was set at 400°C to avoid technetium and rhenium loss by volatilizing. The second stage of the analytical procedure environmental solid sample involves extraction/dissolution after incineration with a mixture of HCl and H₂O₂. Under this condition technetium and rhenium both are soluble the heptavalent state (TcO₄⁻, ReO₄⁻). Ferric ion and NH₃ were added for a ferric hydroxide to remove a number of potentially interfering radionuclides and matrix components. In concentrated hydrochloride acid, technetium is reduced from the heptavalent to tetravalent (such as TcCl₆⁻). Therefore in each step of analysis, hydrogen peroxide is used as oxidant to keep Rhenium and Technetium in heptavalent state and prevent them co-precipitating with ion. Losses of both pertechnetate and perrhenate in these stages are small and similar. Harvey et al. have found that the technetium and rhenium recoeries are consistent with one another. Hence, rhenium is used to be a tracer and rhenium recovery represents technetium recovery. The concentration variations of rhenium in sample treatment are measured by inductively coupled plasma- mass spectroscopy. The recovery of rhenium during separation/purification stages is given by:

$$\text{Recovery} = \frac{\text{Rhenium after stage}}{\text{Rhenium before stage}}$$

“Rhenium” means the amount of rhenium in sample mixture. For the filtration stage, the recoveries of environmental samples, including water, soil and vegetation, are all near 100%. The recoveries of rhenium for soil and vegetation samples for Iron hydroxide scavenge stage are listed in table 1.

Table 1. The recovery of rhenium during the iron hydroxide scavenge stage

Sample	Iron hydroxide scavenge
Soil – tainan	0.907
Vegetation – tea leaves	0.837

The uptake rate of rhenium or technetium for Technetium Rad Disk extraction is given by:

$$\text{Uptake rate} = \frac{(\text{M before extraction} - \text{M after extraction})}{\text{M before extraction}}$$

M means the concentration of rhenium or technetium in sample mixture. The activity of technetium-99 is determined by liquid scintillation counter. The uptake rates are shown in table 2.

Table 2. The uptake of rhenium and technetium for Technetium Rad Disk extraction

Samples	Rhenium	Technetium
Shihmen dam water	>99.99%	~100%
Ditch water	99.96%	~100%
Deep well underground water	99.97%	~100%
Soil – tainan	99.98%	98.08%
Vegetation – tea leaves	99.95%	96.04%

As data in table 2 indicate, the rhenium is satisfactory to be the tracer of technetium in the extraction of Technetium Rad Disk. The tracers for the analysis of technetium-99 include technetium-95m, technetium-97m, technetium-99m and stable rhenium. Harvey et al. have reported the use of rhenium as a yield monitor for the analysis of technetium-99 in soil, biota, seawater and milk. Rhenium offers several advantages- mass carrier, no interference problem, low cost, high purity, constant availability, and simplicity of handling relative to other isotope tracers.

The relationship of counting efficiencies with rhenium contents in the Technetium Rad Disks is described in table3. The counting efficiency of low background gas proportional counter (GPC) is decreasing with rhenium content added to sample. But there is no effect to liquid scintillation counter. Hence, liquid scintillation counter (LSC) is preferred even its background is higher.

Rhenium loading	0.5mg	0.6mg	3mg
Efficiency of GPC	30.1%	29.0%	24.1%
Efficiency of LSC	65.2%	66.3%	65.4%

The detection limit for the procedure was calculated as shown. Assuming a measurement time of 100 minutes, a background count rate of 6cpm, counting efficiency of 65% and a recovery of 100%. Then the minimum activity (MACC) based a critical is given by:

$$\text{MACC} = F \times k \times (2N)^{0.5}$$

Where N – number of background count,

k – a factor dependent upon the probability requirements for not being in error obtained from tables of one-tailed Gaussian distribution data (for a probability < 0.05, k = 1.645),

F – a factor converting to activity.

Thus

$$\text{MACC} = \frac{1.645 \times (2 \times 100 \times 5)^{0.5}}{0.65 \times 1.00 \times 100 \times 60} = 0.0133 \text{ Bq}$$

$$\text{and LOD} = 3 \times \text{MACC} = 0.0399 \text{ Bq}$$

The procedures have been tested with dry vegetation and soil up to 20g. With suitable adjustments to pretreatment stage there is no reason why larger quantities of samples could not be handled successfully.

Conclusion

1. Rhenium may be used as a reliable yield monitor for technetium in the analysis of the environmental samples by being careful of their redox behaviors.
2. Liquid scintillation counter used to determine technetium-99 is preferred because of the stability of efficiency.

3. Technetium Rad Disks are satisfactory used to catch technetium from environmental sample solutions.

Reference

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