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Introduction

Technetium-99 (^{99}Tc) is an important fission product which has been widely distributed in the environment as a result of fallout from nuclear weapons testing¹⁻⁴⁾ and discharges from nuclear facilities^{5,6)}. Measurements of ^{99}Tc are of special interest because of the high mobility of Tc in the environment, its long half-life ($T_{1/2} = 2.11 \times 10^5$ y) and potential long-term radiological consequences.

In order to improve our understanding of the behavior of ^{99}Tc in the environment and to develop appropriate radioactive waste storage/disposal options, it is essential that we obtain more reliable information on the levels, distributions and fate of ^{99}Tc in the environment. It is known that there are several sources of ^{99}Tc in the environment, mainly, reprocessing plants and nuclear weapons test sites. One of the sites is the northern Marshall Islands where the United States carried out over 60 nuclear test detonations during the 1950's. Total carbonate contents of the soil samples are higher than those of normal terrestrial soils. Thus, a separation method for Tc which suits the characteristics of these samples is necessary.

In this study, soil samples collected from various sites in the Marshall Islands were used to evaluate different techniques for the extraction of ^{99}Tc from soil matrices for the determination of ^{99}Tc by inductively coupled plasma mass spectrometry (ICP-MS).

Experimental

Sample and reagents.

Soil samples used in this study were collected from the Marshall Islands between 1992 and 1996 by the Lawrence Livermore National Laboratory (LLNL). The details of

the soil preparation were reported elsewhere⁷). Nitric acid was ultrapure-analytical grade (Tama Chemicals, AA-100). Deionized water (>18 M Ω) was obtained from Milli-Q water system (Millipore Co.). Pre-packed columns of Tc-selective chromatographic resin, TEVA (Ehchrom Industries, Inc.) were used for separations of Tc. A standard ⁹⁹Tc solution available from Amersham (solution TCZ.44) was used for calibrating the ICP-MS. Technetium-95m ($T_{1/2} = 61$ d) was prepared by irradiation of Nb in a cyclotron to be used as a yield monitor⁸).

Chemical separations

Three Tc extraction techniques were examined as shown in Fig. 1. Each solution obtained by the extraction procedures was adjusted to 0.1 M HNO₃ and passed through a TEVA resin column to purify and concentrate Tc isotopes⁹. Because ICP-MS cannot differentiate between ⁹⁹Ru and ⁹⁹Tc, it is necessary to remove all Ru from the final sample solution prior to ICP-MS measurement. Ruthenium present in the sample solution is not effectively retained on the TEVA resin. More than 95% of Ru passes directly through the column with the solution. The column was then washed with 2 M HNO₃ to remove any remaining trace Ru. Technetium was eluted with 5 mL of 8 M HNO₃. By the separation steps, Ru was completely; only < 0.1% of the element was found in the 8 M HNO₃ eluate. The strip solution containing Tc was evaporated to dryness, and the residue dissolved in 5 mL of 2% HNO₃.

Measurement

The chemical recovery was measured by counting ^{95m}Tc in the sample on an NaI (TI) scintillation counter (Aloka, ARC-380) and comparing the results with standard solutions. The ⁹⁹Tc content of the sample solution was then determined by ICP-MS (Yokogawa, PMS-2000) with 180 s counting time 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.

Results and Discussion

ICP-MS is applicable for the measurement of long-lived radionuclides, if the total elemental concentration in the solution is less than 1000 mg/L due to instrumental limitation. A lower total elemental concentration than 300 mg/L is preferable for stable

operation of the instrument. Thus, ranges of element concentrations were measured by ICP-MS in final Tc column eluted solutions from seven separate soil samples using each of the three extraction methods (M1, M2 and M3). The results are shown in Fig. 2. The recovery of matrix elements Na and Al were also very similar between each of the extraction methods. Interestingly, consistently higher concentrations of Ca, Cu, Nb, Mo, I and U were observed in M2 eluates where soils were leached with nitric acid without any prior treatment. It is not clear why we observed consistently higher levels (1-2 orders of magnitude) of matrix elements in the final sample solution using this extraction technique. High levels of dissolved solids in sample solutions may cause matrix induced interferences, and lead to poor instrument stability and suppression of the analyte signal. Thus, M2 extraction technique is less suited for ^{99}Tc measurement by ICP-MS. We therefore suggest that careful attention should be given to the type of extraction procedure used, and the preparation of the sample load solution used for the separation of ^{99}Tc on TEVA columns. For example, the elution characteristics of the TEVA column may have been affected by the presence of small residual quantities of organic material because, unlike M2 soils, the M1 and M3 extracts were both prepared from ashed and/or combusted materials. No interference of ^{98}MoH on the determination of ^{99}Tc by ICP-MS was observed in this study.

Total chemical recoveries of Tc for extraction techniques M1, M2 and M3 were 49.6-98.5%, 39.7-76.4% and 7.6-16.9%, respectively (Fig. 3). M3 extraction method appeared to show that Tc is not very efficiently volatilized from Marshall Islands soils. Probably, due to the high carbonate contents in the samples, Tc was trapped in the molten sample during heating like an alkaline fusion condition. From the results, we judge M1 to be the best method among the studied separation methods. However, we found that the use of a combustion apparatus offers significant advantages over acid dissolution techniques for other soil types/elements. We plan to continue to optimize the technique for routine analyses of ^{99}Tc . Sample volatilization techniques are not critically dependent on sample size, and they help to improve the effectiveness of the following separation by drastically reducing the total dissolved solids content of the sample load solutions.

The concentrations of ^{99}Tc in the seven soil samples collected from the Marshall Islands as determined by M1 and M2 ranged from 0.1 to 1.1 mBq/g dry weight¹⁰. Using a reference date of 1954 the $^{99}\text{Tc}/^{137}\text{Cs}$ activity ratios in Bikini surface soils ranged from 0.7 - 1.1×10^{-4} or around 50 - 70% of the theoretical fission yield production ratio of 1.4×10^{-4} . The residual levels of radionuclides retained in surface soils of the Marshall Islands will depend on the initial inputs, their half-lives and environmental behaviors of the

radionuclides. However, at this time we have no information on the distribution of ^{99}Tc in soil profiles, on the rates of ^{99}Tc transport into underlying ground waters nor on ^{99}Tc transfer factors into plants or organisms. Based on this initial assessment, we can state that persistent levels of ^{99}Tc are being retained in surface soils of the atoll, and that removal rates of ^{99}Tc and ^{137}Cs in surface soils are occurring on similar time-scales. More studies are required to address any possible long-term radiological issues related to ^{99}Tc -particularly developing an understanding of Tc cycling, rates of transport, and uptake factors into native plants and/or organisms.

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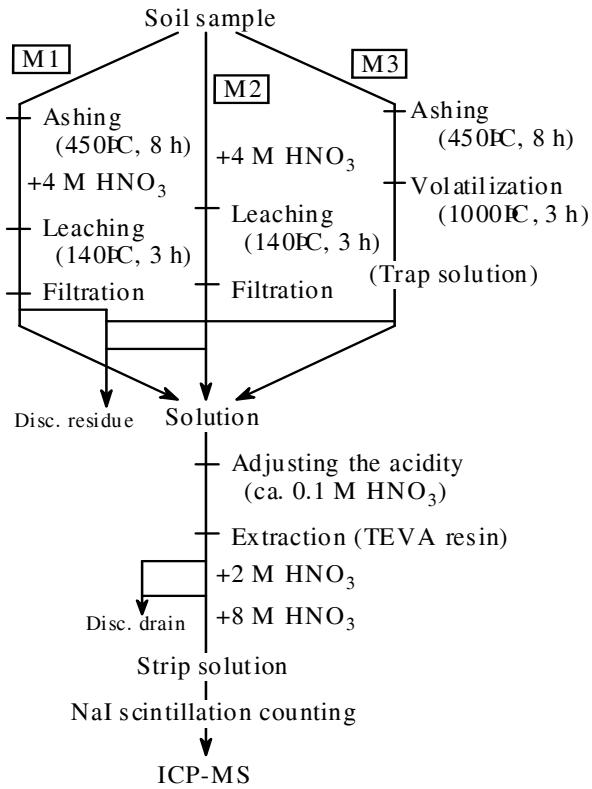


Fig. 1. Schematic diagram of separation methods, M1, M2 and M3, for Marshall Island soil samples.

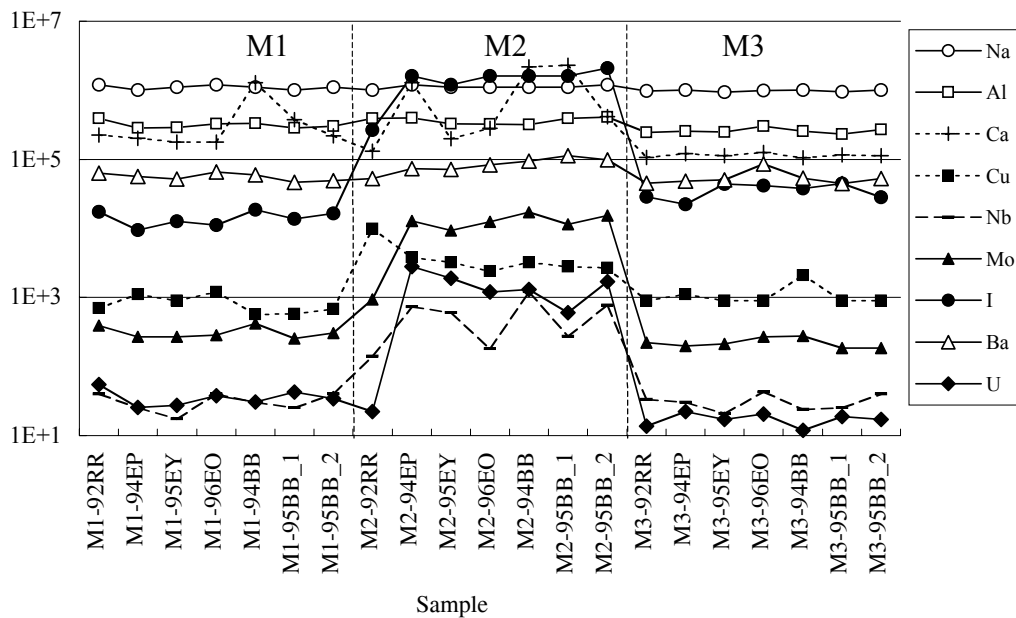


Fig. 2. Concentrations of Na, Al, Ca, Cu, Nb, Mo, I, Ba and U in final solutions for ICP-MS analyzed by M1, M2 and M3.