Separation and Determination of Technetium-99 in Spent PWR Nuclear Fuels

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Received August 2, 2003

Key Words : Technetium, Ruthenium, Spent nuclear fuel, AG MP-1, ICP-MS

Technetium-99, which is formed by the thermal neutron fission of ^{235}U and ^{239}Pu, is a beta emitter with a long half-life of 2.1×10^5 years. As a part of the determination of the nuclide inventories for the spent nuclear fuels, quantification of ^{99}Tc, using chemical methods, is necessary. The content of ^{99}Tc in the spent pressurized water reactor (PWR) fuel with a burn-up of 35,000 MWD/MtU (megawatt-day per metric ton of uranium), after a cooling period of 10 years, is estimated at about 800 g per ton of uranium.[1]

Technetium-99 in the spent nuclear fuel solutions can be measured by beta counting after the elimination of other radioactive nuclides. However, the complete removal of them to eliminate their interference with the beta counting of ^{99}Tc is nearly impossible by a single use of any separation method due to the differences in the behavior of the several elements in the separation stage. Inductively coupled plasma-mass spectrometry (ICP-MS) has been used as an alternative to beta counting for the determination of ^{99}Tc in environmental and radioactive waste samples. ICP-MS demands the elimination of ^{99}Ru, which is the only isobaric nuclide present in the spent nuclear fuels. The separation and purification of ^{99}Tc from the other radioactive nuclides are also required to prevent the contamination of the ICP-MS.

In our previous work,[2] the study on the separation and beta counting of ^{99}Tc in the simulated samples was conducted for the LiCl molten salt process, converting uranium dioxide of the spent PWR fuels to uranium metal. In continuation of that work on the analysis of ^{99}TC, the ICP-MS quantification method for ^{99}Tc in spent PWR nuclear fuels dissolved in nitric acid is described in the present paper. The chromatographic separation of ^{99}Tc from the spent nuclear fuel solutions was accomplished using a macro-porous anion exchange resin, AG MP-1.

Experimental Section

Reagents and instruments. Analytical grade reagents and deionized water were used throughout this study. $K_2RuNOCl_5$, KIO_4 and nitric acid were purchased from the Aldrich Chemical Co., USA. A mixed metal solution of U(VI), Ru(III), Mo(VI), Zr(IV), La(III), Sr(II), and Ba(II) was prepared by combining an appropriate aliquot of each of the Spex Certipre solutions (Metuchen, USA), evaporating them to incipient dryness, and dissolving the residue in 0.5 M HNO$_3$. Anion exchange resin, AG MP-1 (200-400 mesh) in chloride form was used for the experiments. The aqueous

solution of ammonium pertechnetate, of which the ^{99}Tc purity was more than 99%, was obtained from the An Eckert & Ziegler Co., USA. Insta-gel XF (Packard) was used as a scintillator in the liquid scintillation counting.

An ICP-AES (Thermo Jarrell Ash IRIS HR) installed in a stainless steel glove box was used to analyze the radioactive samples.[3] Beta counting was made using a Packard 2500TR/AB, TRI-CARB liquid scintillation counter (LSC). ICP-MS measurements were made with a high resolution type ICP-MS (Finnigan MAT, ELEMENT). The gamma activities were measured by a gamma spectrometric system (EG & G ORTEC, ADCAM100) with a HPGe detector (EG & G ORTEC, GMX30195-P). The detector had the counting efficiency of 30% and a FWHM (full width at half maximum) of less than 2 keV for the 1330 keV line of ^{60}Co.

Decomposition and oxidation of RuNO^{3+}. Nitrosyl-ruthenium solutions of 6.0×10^{-4} M $K_2RuNOCl_5$ were prepared by dissolving an appropriate amount of solid $K_2RuNOCl_5$ in nitric acid solutions with varying concentrations. An aliquot of 0.25 M KIO_4, with varying IO_4^-/RuNO^{3+} mole ratios from 5 to 30, was added to the ruthenium solution. The solution was left to stand overnight in the air, after which its ruthenium concentration was determined by ICP-AES.

Dissolution of the spent PWR fuel samples. A known amount of a spent nuclear fuel sample (0.5-1 g) was refluxed for more than 18 h in 40-50 mL of 8 M HNO$_3$. Just after dissolution of the spent fuel sample and its cooling, the resulting spent fuel solution was filtered through a glass fiber filter (Whatman, GF/F, 0.7 μm) and the filtrate (hereafter called the "spent fuel solution") was stored in a polyethylene bottle.

Ion exchange of metals. A 7×25 mm AG MP-1 column in a 7 mm (i.d.) polyethylene tube was prepared by the slurry-packing method. A plug of glass wool was placed below and on top of the resin. The column was washed with 5 M HNO$_3$ to convert the resin to the NO$_3$-form and then it was washed sufficiently with deionized water. Following these procedures the column was preconditioned before use by passing 3 mL of 0.5 M HNO$_3$ through it.

Appropriate aliquots of the mixed metal solution and the solution of TcO$_4^-$ were combined in 0.5 M nitric acid, and then loaded into the resin column. Ten milliliters of 1 M HNO$_3$ and 10 mL of 10 M HNO$_3$ were sequentially passed through the column. The effluent was collected fractionally, and the concentrations of ^{99}Tc and the other metals in each fraction were determined by LSC and ICP-AES, respec-

tively. In the entire separation stages, the flow rate was maintained at about 0.3 mL/min, using gravity flow.

Analyses of the spent fuel samples. One drop (about 10 μL) of 0.1 M KIO$_4$ solution was added to an aliquot of the spent fuel solution after which the solution was allowed to stand overnight. After adjusting the nitric acid concentration of the solution to 0.5 M, one drop of ethanol was added. The resulting solution was loaded into the column as described above. After washing the column with 10 mL of 1 M HNO$_3$, technetium was eluted with 10 mL of 10 M HNO$_3$. One half milliliter portion of 10 M HNO$_3$ effluent (hereafter called "^{99}Tc eluate") was taken and diluted to 10 mL with deionized water followed by the measurement of ^{99}Tc, using ICP-MS.

Results and Discussion

Valence control of Ru and Tc. Technetium and ruthenium produced from the fission of uranium have been known to exist as a form of alloy in spent PWR nuclear fuels.[4] The spent fuel samples were dissolved in concentrated nitric acid, using a reflux system to prevent the loss of technetium as volatile technetium heptoxide. During the dissolution of the spent nuclear fuel in nitric acid, technetium and ruthenium form the pertechnetate (TcO$_4^-$)[5] and the nitrosyl-ruthenium (RuNO^{3+}) complexes, respectively, which can be expressed as the general formula[6,7] [RuNO(NO$_2$)$_m$(OH)$_n$]$^{3-(m+n)}$. A large fraction of the nitrato complexes of RuNO^{3+} exists as anionic complexes that are strongly adsorbed on the anion exchange resins. Therefore, before sample loading the RuNO^{3+} should be decomposed and converted to the non-adsorbable ruthenium species. In the previous paper,[2] we proposed a combination of sodium hypochlorite and ethanol for the valence control of ruthenium in hydrochloric acid media. However, in the preliminary experiments sodium hypochlorite was found to be ineffective in the decomposition and oxidation of RuNO^{3+} to ruthenium tetroxide (RuO$_4$) in nitric acid media. It is well known that RuNO^{3+} is very stable and is not readily oxidized by the powerful oxidizing agents such as KMnO$_4$, NaBiO$_3$ and K$_2$S$_2$O$_8$.[8] In this study, to convert nitrosylruthenium complexes to the nonadsorbable species in the anion exchange resin (AG MP-1), RuNO^{3+} was decomposed and oxidized to RuO$_4$ with potassium periodate (KIO$_4$), and the RuO$_4$ was subsequently reduced to Ru^{3+} using ethanol. Due to its volatility, a large fraction of the ruthenium tetroxide escaped from the solution before its reduction by ethanol. Based on the ICP-AES analysis of ruthenium in the nitric acid solutions of K$_2$RuNOCl$_5$ before and after the addition of KIO$_4$, we found that the conversion of RuNO^{3+} to RuO$_4$ proceeded in the order 3 M < 5 M < 8 M, with an increase in the concentration of nitric acid. Considering this result and the nitric acid concentration of the spent fuel solutions, we concluded that 8 M HNO$_3$ was the suitable medium for the conversion of RuNO^{3+} to RuO$_4$ using KIO$_4$. Although the oxidation reactions of KIO$_4$ are known to be very slow in dilute solutions,[8,9] we found that the oxidation rate for RuNO^{3+} increased rapidly
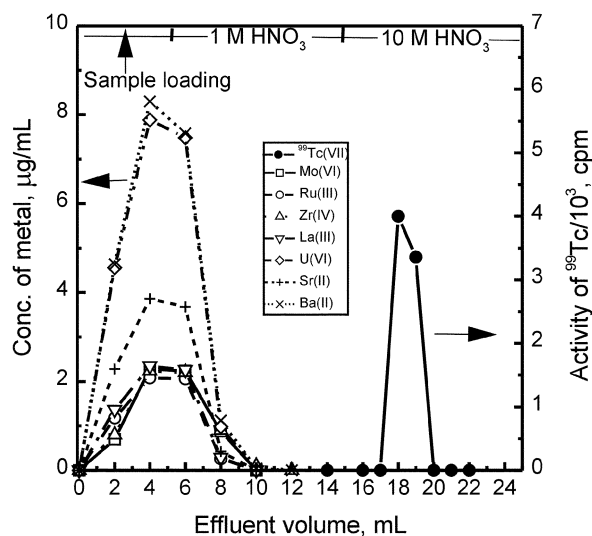

Figure 1. Separation of technetium from uranium and fission product metals on anion exchange resin. Bed; 7(i.d.) $\times$ 25 mm. Resin; AG MP-1 (200-400 mesh). Loading amounts; 113 μg of fission product elements, 40 μg of U(VI) and 3.4 nCi of ^{99}Tc(VII) in 5.0 mL of 0.5 M HNO$_3$. Wash solution; 10 mL of 1 M HNO$_3$. Eluent of Tc; 10 mL of 10 M HNO$_3$.

with increasing amounts of KIO$_4$. Thus, in the case of the K$_2$RuNOCl$_5$ solution of 8 M HNO$_3$, RuNO^{3+} was completely oxidized to RuO$_4$ about 24 h after the addition of amounts of KIO$_4$ greater than 5 times the moles of RuNO^{3+}. In accordance with earlier work,[2] the RuO$_4$ remaining in the nitric acid solutions was reduced to Ru^{3+}, using ethanol in 0.5 M HNO$_3$.

Optimization of the Tc separation procedure. To investigate the chromatographic behavior of uranium and the fission product elements, 5 mL of the synthetic metal solution in 0.5 M HNO$_3$ was applied to the column followed by its washing with 10 mL of 1 M HNO$_3$ and 10 M HNO$_3$ in series. The amounts of loaded metals were 0.2 μg (3.4 nanocuries) of ^{99}Tc(VII), 40 μg of U(VI), 20 μg of Sr(II), 42.5 μg of Ba(II), and 12.5 μg each of Mo(VI), Ru(III), Zr(IV) and La(III). As seen in Figure 1, large fractions of uranium and the fission product elements, except technetium, passed through the column during sample loading and the remainder was washed off the column with 1 M HNO$_3$. On the other hand, technetium was completely held as TcO$_4^-$ by the resin at the sample loading stage and was not removed by the 1 M HNO$_3$ wash. But the technetium was readily removed by less than 5 mL of the 10 M HNO$_3$ eluent. Thus, 10 mL of 10 M HNO$_3$ was sufficient to recover completely the technetium from the column. No technetium was found in the 10 mL effluent of 1 M HNO$_3$. Moreover, uranium and the other fission product elements were not found in the ^{99}Tc eluate by ICP-AES, which confirms their complete removal from the resin column by the 1 M HNO$_3$ washing step.

To determine the degree of purification of ^{99}Tc from radioactivity, gamma activity measurements were performed for the loading sample of the spent fuel solution and its ^{99}Tc eluate. We observed that the gamma activity of ^{99}Tc eluate

Table 1. Analytical results for ^{99}Tc in the spent PWR fuels

Burnup of fuel (MWD/MtU)	Sample	Conc. of ^{99}Tc (μg ^{99}Tc/g U)	
		Measured	Expected
28,000	1	674	
	2	682	
	3	688	
	Average	681	667
	Std. dev.	7	
36,000	1	864	
	2	881	
	3	875	
	Average	873	875
	Std. dev.	9	

was slightly greater than that of the blank solution of 10 M HNO$_3$, and that the separation resulted in a decrease in the sum of the gamma counts by a factor of 1/2000. The decontamination factor (D.F.) of a nuclide was defined as a nuclide concentration in the sample solution divided by the concentration in the ^{99}Tc eluate. For some gamma active nuclides the D.F.'s were calculated to be 170, 68000, 260, and 5000 for ^{241}Am, ^{137}Cs, ^{95}Zr, and ^{140}La, respectively. These results indicate that the anion exchange procedure can provide a satisfactory degree of decontamination of the technetium from other radioactive nuclides for the ICP-MS of ^{99}Tc.

Analyses of the spent fuel samples. The validity of the proposed procedure was assessed by determining the amount of ^{99}Tc in three samples from each of the spent PWR fuel solutions. The calibration plot of ICP-MS data gave a good straight line with a near-zero intercept and a coefficient of a linear correlation of 0.9999 over 0.1-0.5 ng for the ^{99}Tc/ mL concentration range. The peak area at the mass 101 for ^{101}Ru, whose concentration is similar to that of ^{99}Tc for a burn-up of 36,000 MWD/MtU, was found to be negligible compared with that of ^{99}Tc, indicating a near complete elimination of ruthenium from the ^{99}Tc eluate. The measured concentrations of ^{99}Tc are shown in Table 1. The expected values calculated using ORIGEN 2[10] (which is a computer code for calculating the nuclide compositions and characteristics of nuclear materials) on the basis of the burn-up of the nuclear fuels are also included in Table 1 for comparison.

The determined average concentration, 873 μg ^{99}Tc per gram of spent fuel uranium, agrees well with the expected concentration of ^{99}Tc of 875 μg for the spent fuel with a burn-up of 36,000 MWD/MtU. In the case of the spent fuel with a burn-up of 28,000 MWD/MtU, the average concentration was determined to be 2.1% higher than the expected concentration. Considering the many difficulties of sampling, weighing, and dilution by remote-control operation in a hot cell, uncertainties of less than 5% are accepted as satisfactory in the chemical analysis of spent nuclear fuel samples.

We have concluded from the present study that ^{99}Tc can be separated with high recoveries from the nitric acid solutions of spent PWR nuclear fuels with AG MP-1 anion exchange chromatography and accurately determined by ICP-MS.

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