

Rapid Radiochemical Analyses in Support of Fukushima Nuclear Accident – 13196

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ABSTRACT

There is an increasing need to develop faster analytical methods for emergency response, including emergency soil and air filter samples [1, 2]. The Savannah River National Laboratory (SRNL) performed analyses on samples received from Japan in April, 2011 as part of a U.S. Department of Energy effort to provide assistance to the government of Japan, following the nuclear event at Fukushima Daiichi, resulting from the earthquake and tsunami on March 11, 2011. Of particular concern was whether it was safe to plant rice in certain areas (prefectures) near Fukushima.

The primary objectives of the sample collection, sample analysis, and data assessment teams were to evaluate personnel exposure hazards, identify the nuclear power plant radiological source term and plume deposition, and assist the government of Japan in assessing any environmental and agricultural impacts associated with the nuclear event. SRNL analyzed approximately 250 samples and reported approximately 500 analytical method determinations. Samples included soil from farmland surrounding the Fukushima reactors and air monitoring samples of national interest, including those collected at the U.S. Embassy and American military bases. Samples were analyzed for a wide range of radionuclides, including strontium-89, strontium-90, gamma-emitting radionuclides, and plutonium, uranium, americium and curium isotopes. Technical aspects of the rapid soil and air filter analyses will be described.

The extent of radiostrontium contamination was a significant concern. For $^{89,90}\text{Sr}$ analyses on soil samples, a rapid fusion technique using 1.5 gram soil aliquots to enable a Minimum Detectable Activity (MDA) of $<1 \text{ pCi } ^{89,90}\text{Sr/g}$ of soil was employed. This sequential technique has been published recently by this laboratory for actinides and radiostrontium in soil and vegetation [3, 4]. It consists of a rapid sodium hydroxide fusion, pre-concentration steps using iron hydroxide and calcium fluoride precipitations, followed by Sr-Resin separation and gas flow proportional counting. To achieve a lower detection limit for analysis of some of the Japanese soil samples, a 10 gram aliquot of soil was taken, acid-leached and processed with similar preconcentration chemistry. The MDA using this approach was $\sim 0.03 \text{ pCi/g}$ (1.1 mBq/g), which is less than the $0.05\text{-}0.10 \text{ pCi/g } ^{90}\text{Sr}$ levels found in soil as a result of global fallout. The chemical yields observed for the Japanese soil samples was typically 75-80% and the laboratory control sample (LCS) and matrix spike (MS) results looked very good for this work. Individual QC results were well within the $\pm 25\%$ acceptable range and the average of these results does not show significant bias. Additional data for a radiostrontium in soil method for 50 gram samples will also be presented, which appears to be a significant step forward based on looking at the current literature, with higher chemical yields for even larger sample aliquots and lower MDA [5, 6, 7]

Hou et al surveyed a wide range of separation methods for Pu in waters and environmental solid samples [8]. While there are many actinide methods in the scientific literature, few would be considered rapid due to the tedious and time-consuming steps involved. For actinide analyses in

soil, a new rapid method for the determination of actinide isotopes in soil samples using both alpha spectrometry and inductively-coupled plasma mass spectrometry was employed. The new rapid soil method utilizes an acid leaching method, iron/titanium hydroxide precipitation, a lanthanum fluoride soil matrix removal step, and a rapid column separation process with TEVA Resin. The large soil matrix is removed easily and rapidly using these two simple precipitations with high chemical recoveries and effective removal of interferences. [9, 10] Vacuum box technology and rapid flow rates were used to reduce analytical time. Challenges associated with the mineral content in the volcanic soil will be discussed.

Air filter samples were reported within twenty-four (24) hours of receipt using rapid techniques published previously. [11] The rapid reporting of high quality analytical data arranged through the U.S. Department of Energy Consequence Management Home Team was critical to allow the government of Japan to readily evaluate radiological impacts from the nuclear reactor incident to both personnel and the environment.

SRNL employed unique rapid methods capability for radionuclides to support Japan that can also be applied to environmental, bioassay and waste management samples. New rapid radiochemical techniques for radionuclides in soil and other environmental matrices as well as some of the unique challenges associated with this work will be presented that can be used for application to environmental monitoring, environmental remediation, decommissioning and decontamination activities.

INTRODUCTION

The need for rapid analytical methods for environmental radiochemical analyses in response to a terrorist event such as a radiological dispersive device (RDD) or improvised nuclear device (IND) is well-known. The recent incident at Fukushima Nuclear Power Plant in March, 2011 reinforces the need to have rapid analyses for radionuclides in environmental samples. There are a number of methods reported in the literature to determine actinides and strontium isotopes in environmental samples, but often the methods are not rapid or have mediocre to poor chemical yields, indicating poor method performance.

Hou et al. [8] surveyed a wide range of separation methods for Pu in waters and environmental solid samples. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40-85% and many of the methods noted are very time-consuming. Salminen et al reported a method for determining plutonium in air filters using UTEVA Resin plus TRU Resin (Eichrom Technologies, Lisle, IL, USA). [12] The authors were interested in leachable plutonium so a less rigorous acid leach was used. Refractory particles that could be present from a RDD or IND would not likely be digested using this method in an emergency.

Vajda and Kim provide a very good overview of recent radiostrontium separation and analytical measurement techniques. [6] This review also included more classical methods using fuming nitric precipitation as reported by Bojanowski et al [13]. Fuming nitric acid presents handling difficulties and can be very tedious and time-consuming. Wang et al. [14] reported a sequential method to determine actinides and strontium in soil samples. The chemical recoveries

using this method on NRIP (National Institute of Standards and Technology [NIST] Radiochemistry Intercomparison Program) soil for strontium were 63-77%. A large number of sequential steps were required, but the accuracy of the results versus the NIST reference values was very good. Čerenkov counting, while it offers benefits regarding selectivity against low energy beta emitters and allows for rapid measurement of ^{89}Sr , has a much higher MDA than gas flow proportional counting. This allows smaller aliquots/and/or shorter count times to be used. In addition, gas flow proportional counters can be used in a simultaneous counting mode instead of sequential mode, minimizing analysis time and increasing sample throughput.

In contrast to many of the methods in the literature, the Savannah River National Laboratory has developed many rapid radiochemical methods that can be used in an emergency or for routine analyses. This expertise was critical in providing rapid analytical results to assist the government of Japan in the aftermath of the Fukushima incident in March, 2011.

RESULTS and DISCUSSION

The Savannah River National Laboratory performed analyses on samples received from Japan in April, 2011 as part of a U.S. Department of Energy effort to provide assistance to the government of Japan. Of particular concern was whether it was safe to plant rice in certain areas (prefectures) near Fukushima. Gamma analyses were performed using a high purity germanium detector, with gamma libraries tailored to mixed fission products and appropriate parent-daughter relationships. Rapid Sr-89/90 analysis was of particular concern regarding the planting of rice, which was to occur within two to three weeks of sample receipt.

Two different analytical techniques were employed in the Savannah River Environmental Laboratory to determine $^{89,90}\text{Sr}$ in Japanese soil samples very rapidly. A United States Department of Agriculture (USDA) permit to receive foreign soil had to be obtained very quickly to prepare for receipt of the Fukushima soil samples. The capabilities discussed below illustrate some of the unique rapid analysis capabilities at Savannah River National Laboratory that can be a national asset in times of radiological emergencies.

Figure 1 shows the rapid fusion technique using 1.5 gram soil aliquots to enable a MDA (Minimum Detectable Activity) of $<1 \text{ pCi } ^{89,90}\text{Sr/g}$ of soil that was employed. This sequential technique has been published recently by this laboratory for actinides and radiostrontium in soil and vegetation [8, 9]. It consists of a rapid sodium hydroxide fusion, pre-concentration steps using iron hydroxide and calcium fluoride precipitations, followed by Sr-Resin separation and gas flow proportional counting.

Figure 2 shows the sample preparation method employed for Sr-89/90 in large sample aliquots. To achieve a lower detection limit for analysis of certain soil samples, a 10 gram aliquot of soil was taken, acid-leached and processed with similar preconcentration chemistry. The MDA using this approach was $\sim 0.03 \text{ pCi/g}$ (1.1 mBq/g), which is less than the $0.05\text{-}0.10 \text{ pCi/g } ^{90}\text{Sr}$ levels found in soil as a result of global fallout. The large amounts of iron in Japanese soil limited the size of soil sample aliquots that could be easily handled to $\sim 10\text{-}15\text{g}$ due to very large iron hydroxide precipitates. The chemical yields observed for the Japanese soil samples shown in Table 1 were typically 75-80% and the laboratory control sample (LCS) and matrix spike (MS) results

looked very good for this work. The first 7 batches were completed with the 1.5g soil method, while the subsequent batches showing lower MDA levels were completed with the 10g soil aliquot method. Figure 3 shows the rapid column separation method used with both sample preparation methods. Small particle size Sr Resin cartridges (Eichrom Technologies, Lisle, IL, USA) were used with rapid flow rates using vacuum box technology.

A newer version of this approach was developed for application to even larger sample aliquots (50 g) from soil samples taken at the Savannah River Site so that very low detection limits can be achieved. The method uses an acid leach, a rapid sample pre-concentration approach and vacuum-assisted column flow rates. The sample analyses required <16 hours to complete, with a significant portion (4 hours or more) of that time being the evaporation of the relatively large leachate solutions. This is still relatively rapid when considers that a 50 gram soil aliquot is being processed. Table 2 shows the measured values for ^{90}Sr in a set of seven 50g soil samples spiked at the 59.2 mBq/g level. The average ^{90}Sr result was $57.8 \text{ mBq/g} \pm 1.7 \text{ mBq}$ (1SD, standard deviation) with an average bias of -2.36%. The average stable Sr carrier recovery was 89.3% (SD =4.7%), indicating very good chemical yield for the method even for 50g sample aliquots. The measured values were corrected for native content in the soil of $1.35 \text{ mBq } ^{90}\text{Sr/g}$. Table 3 shows the measured values for ^{90}Sr in a set of seven 50 g soil samples spiked at the 11.84 mBq/g level. The average ^{90}Sr result was $11.5 \text{ mBq/g} \pm 0.7 \text{ mBq/g}$ (SD). The average stable Sr carrier recovery was 89.6% (SD =2.7%) with an average bias of -2.51%.

Rapid air filter analyses were provided using the recently published SRNL analytical method. [11] In some cases, a second column clean-up using Sr Resin was employed to ensure complete removal of all possible beta interferences, if total beta analysis results were $> \sim 37 \text{ Bq}$. Table 4 shows the QC and matrix spikes recoveries for the air filter samples received. The results indicate an average Sr carrier yield of 85.1% and average LCS result of 94.8%.

Actinide analyses were performed on some of the soil samples, first with a 2 gram rapid fusion method [3] and subsequently with a large sample aliquot method. The Japanese soil contained large amounts of iron, which limited the sample aliquot size that could be taken for actinide analysis. To enable low MDA limits to be achieved, several replicate sample aliquots were processed and recombined after the final actinide fractions were purified. Figure 4 shows a sample preparation technique for plutonium isotopes to eliminate much of the large soil sample matrix similar to what was used in this work. [9, 10] Alpha spectrometry and inductively-coupled plasma mass spectrometry techniques were applied to perform final measurements of actinide isotopes.

The rapid radiochemical analyses provided to the government of Japan and the U.S. Department of Energy provided information that assisted with timely evaluation of personnel exposure hazards, identification of the nuclear power plant radiological source term and plume deposition, and assisted the government of Japan in assessing any environmental and agricultural impacts associated with the nuclear event. SRNL continues to show leadership regarding rapid analytical capabilities that can be extended to other aspects of national security, environmental, and energy mission areas. These rapid analytical techniques can also be applied to decontamination and decommissioning samples and waste processing as well.

SUMMARY

SRNL analyzed approximately 250 samples and reported approximately 500 analytical method determinations to assist the government of Japan. Samples included soil from farmland surrounding the Fukushima reactors and air monitoring samples of national interest, including those collected at the U.S. Embassy and American military bases. Samples were analyzed for a wide range of radionuclides, including strontium-89, strontium-90, gamma-emitting radionuclides, and plutonium, uranium, americium and curium isotopes. The rapid radiochemical methods available at the Savannah River National Laboratory (SRNL) were key to providing rapid reliable soil and air filter analysis data to the U.S. Department of Energy to assist the government of Japan in this time of national crisis.

The rapid analytical work allowed the evaluation of personnel exposure hazards, identification of the nuclear power plant radiological source term and plume deposition, and assisted the government of Japan in assessing any environmental and agricultural impacts associated with the nuclear event.

This effort demonstrates that the rapid methods capability employed by SRNL uniquely positions this laboratory as a national lab of choice for emergency environmental and bioassay analyses in a radiological emergency. In addition, these types of rapid analytical capabilities can be extended to other aspects of national security, environmental, and energy mission areas. These techniques can also be applied to decontamination and decommissioning samples and waste processing as well.

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Table 1 Sr-89/90 Analyses on Fukushima Soil Samples

SOIL Batch	N	Avg. Sr Carrier		% Sr-90 Recovery		Approximate MDC (pCi/g)
		% Recovery	+/- 1 sigma	LCS	MS	
1	14	78.1	9.4	115.5	98.8	1
2	21	71.5	8.5	100.5	89.1	0.9
3	22	74.2	5.1	100.3	94.5	0.8
4	22	79.7	5.3	106.4	98.5	0.7
5	22	82.1	8.8	105.2	91.7	0.7
6	12	74.1	5.8	106.3	107.1	0.8
7	11	77.5	3.8	91.3	109.9	0.4
8	7	77.1	7.6	90.2	108.9	0.05
9	11	86.1	8.4	105.4	94.9	0.05
10	10	71.9	12.5	99.7	97.4	0.05
11	10	76.6	11.7	94.3	94.3	0.04
Avg.		77.2		101.4	98.6	

Table 2 ⁹⁰Sr in Soil Results (59.2 mBq/g level) - 50 g samples

Sample ID	Sr carrier (%)	⁹⁰ Sr Reference Value (pCi g ⁻¹)	⁹⁰ Sr Reference Value (mBq g ⁻¹)	⁹⁰ Sr Measured Value (mBq g ⁻¹)	Difference (%)
1	86.4	1.60	59.2	60.6	2.36
2	93.9	1.60	59.2	54.9	-7.26
3	81.0	1.60	59.2	58.3	-1.52
4	92.5	1.60	59.2	57.7	-2.53
5	87.8	1.60	59.2	57.6	-2.70
6	93.9	1.60	59.2	58.3	-1.52
7	89.8	1.60	59.2	57.2	-3.38
Avg	89.3			57.8	-2.36
SD	4.7			1.7	
% RSD	5.3			2.9	
Measured values corrected for 1.35 mBq ⁹⁰ Sr/g found in unpiked soil					

Table 3 ⁹⁰Sr in Soil Results (11.8 mBq/g level) - 50 g samples

Sample ID	Sr carrier (%)	⁹⁰ Sr Reference Value (pCi g ⁻¹)	⁹⁰ Sr Reference Value (mBq g ⁻¹)	⁹⁰ Sr Measured Value (mBq g ⁻¹)	Difference (%)
1	87.8	0.32	11.84	11.2	-5.41
2	88.4	0.32	11.84	11.9	0.51
3	87.1	0.32	11.84	12.2	3.04
4	93.9	0.32	11.84	12.7	7.26
5	92.5	0.32	11.84	11.2	-5.41
6	87.1	0.32	11.84	10.9	-7.94
7	90.5	0.32	11.84	10.7	-9.63
Avg	89.6			11.5	-2.51
SD	2.7			0.7	
% RSD	3.1			6.4	
Measured values corrected for 1.35 mBq ⁹⁰ Sr/g found in unpiked soil					

Table 4 Sr-89/90 Analyses on Fukushima Air Filter Samples

AF Batch	N	Avg. Sr. Carrier		% Recovery	Approximate MDC (pCi/filter)
		% Recovery	+/- 1 sigma	LCS	
A	14	60.0	15.0	82.5	1 - 2
B	14	92.3	5.3	100.1	1 - 1.5
A`	16	91.1	7.3	88.6	1
B`	16	91.6	4.3	94.6	1
C`	16	92.7	7.3	104.0	1
ARF19	17	79.9	4.7	92.0	0.7
AF/Swipes A	7	93.3	4.0	94.1	0.5
AF/Swipes B	7	80.2	10.7	102.7	0.5
Avg.		85.1		94.8	

for the air filter batches A, B, A`, B` and C` - analyzed only 10 of the 20ml dissolved aliquot

ARF19 used 15 of 20 ml

AF/Swipe batches used the entire sample

Figure 1 Rapid Fusion Method for Sr-89/90 in 1-2g Soil Samples

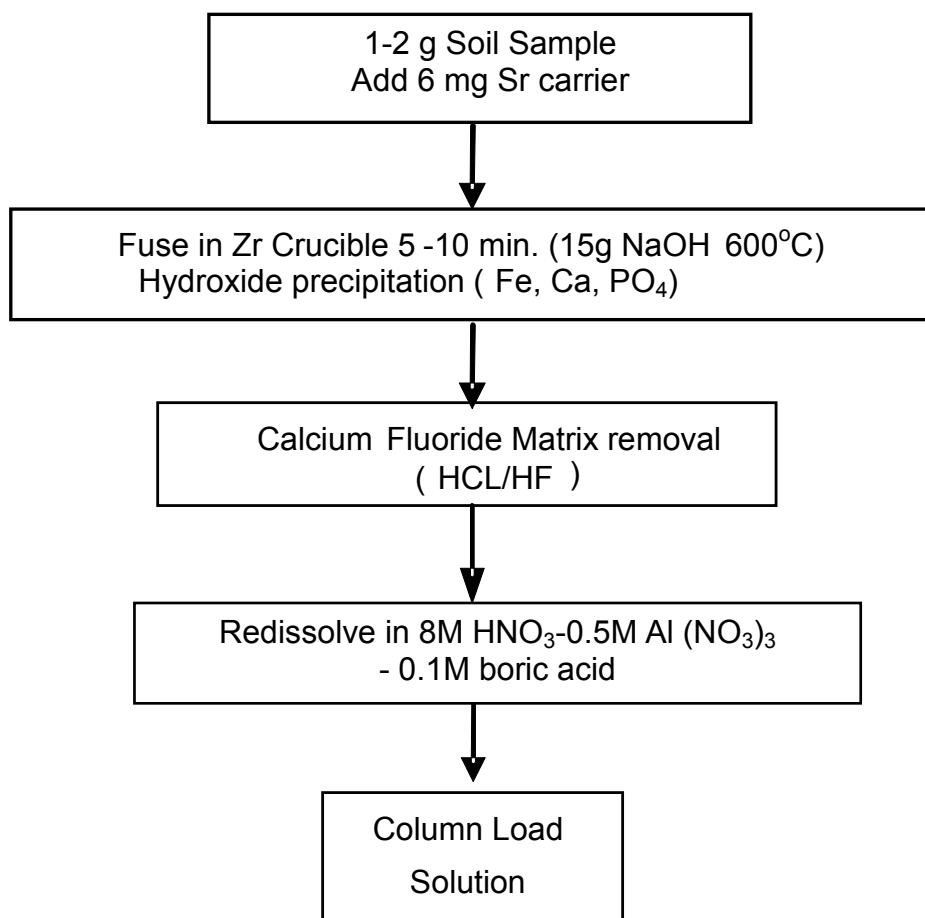


Figure 2 Rapid Sample Preparation Method for Sr-89/90 in Large Soil Samples

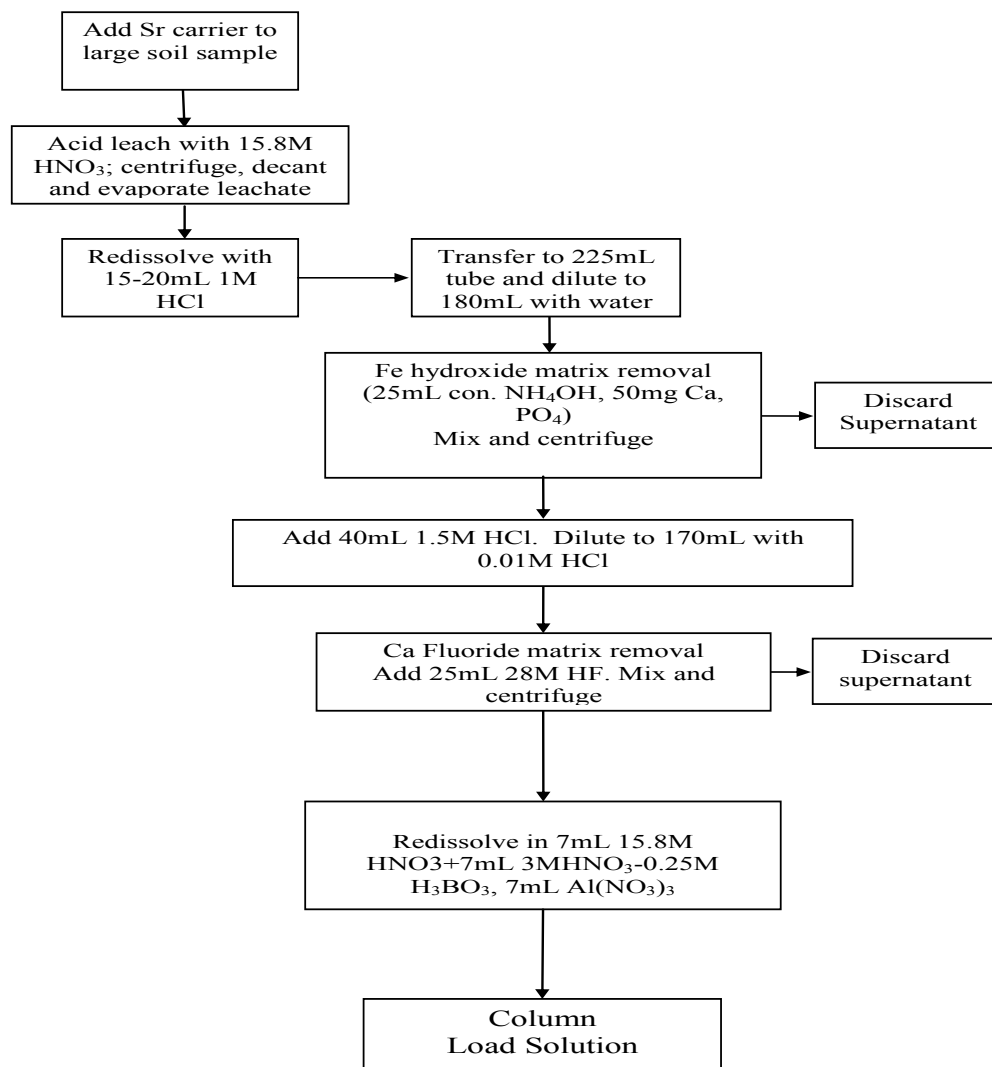


Figure 3 Rapid Column Separation Method for Sr-89/90 in Soil Samples

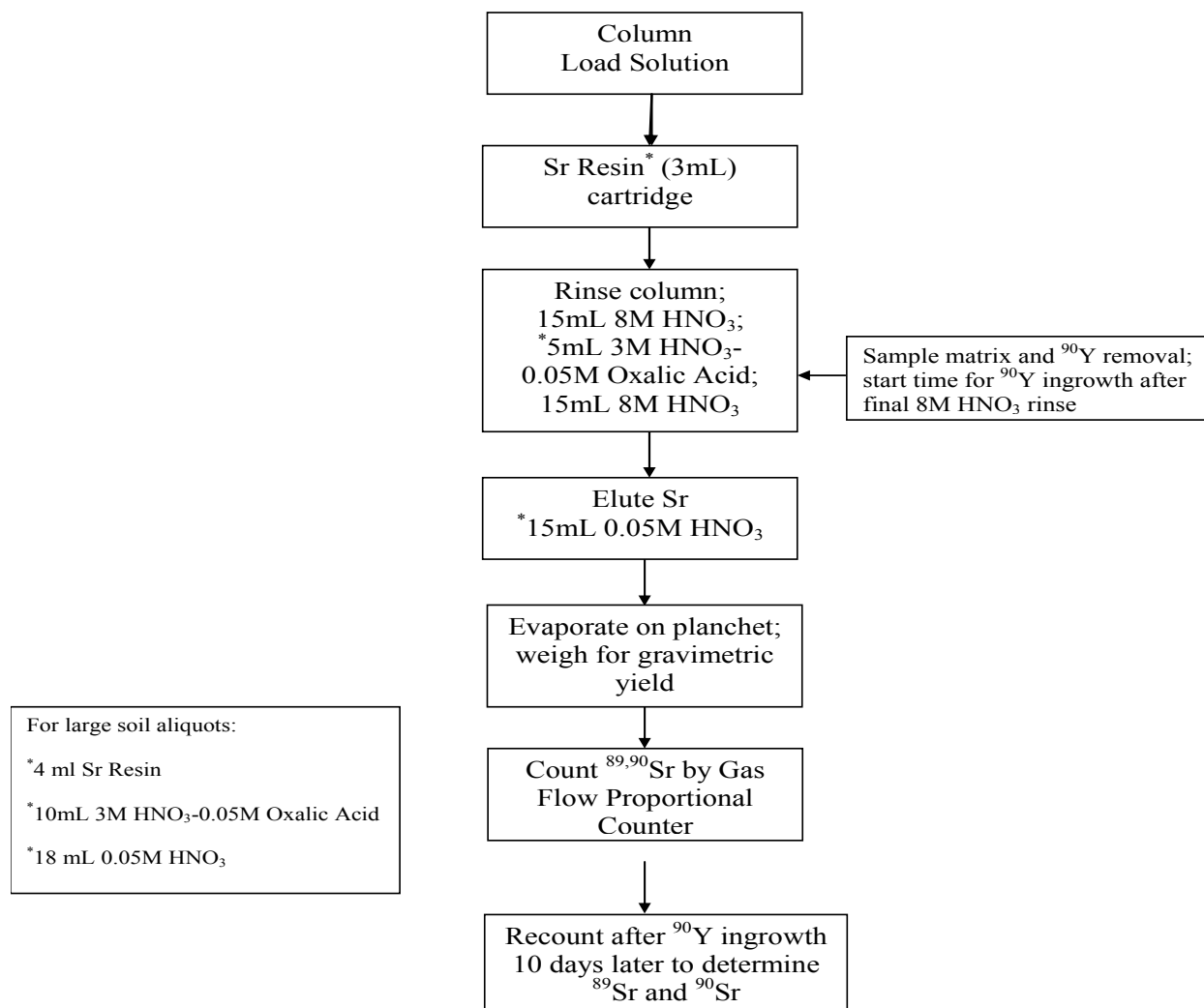


Figure 4 Rapid Sample Preparation Method for Actinides in Large Soil Samples

