

**^{226}Ra BY ALPHA SPECTROMETRY, A COMPARISON OF
PREPARATION AND SEPARATION METHODS
BY TWO INDEPENDENT LABORATORIES**

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ABSTRACT

Accelerated cleanup at Department of Energy (DOE) and United States Army Corps of Engineers (USACE) sites throughout the country have demanded the need for reduced turn-around-times (TAT) for laboratory analytical results. Traditional methods require a significant holding period to allow daughter nuclide ingrowth and accurate quantification of ^{226}Ra activity⁵. Similar precision can be accomplished through alpha spectrometry with a significant reduction in TAT; currently, however, there is no accepted preparation or chemical separation method attached to this analysis technique. Two independent environmental laboratories compared different preparation and separation methods for ^{226}Ra in soil and water matrices. Sample preparation either by digestion in a concentrated acid mixture, or by pyrosulfate fusion using the Sill Method^{1,2,3,4}, both produce accurate alpha spectrometric measures of ^{226}Ra activity.

INTRODUCTION

The current Environmental Protection Agency (EPA) approved method (Method 903.1)⁵ for characterizing the ^{226}Ra activity in environmental samples involves the emanation and subsequent scintillation counting of a daughter product, ^{222}Rn . While accurate, this method requires a 4-8 day ingrowth period to establish equilibrium between the ^{226}Ra and ^{222}Rn activities. When this ingrowth period is added to the time necessary for sample shipment and receipt, priority scheduling, preparation and counting, and final data review and reporting, sample results may not be available until 21-28 days after the initial sampling. In contrast, alpha spectrometry does not require a period of ingrowth, instead measuring the alpha decay of ^{226}Ra directly with chemical yields determined by gamma spectrometry. Because ^{226}Ra by alpha spectrometry does not yet have an accepted preparation and separation method, two independent environmental laboratories measured ^{226}Ra activity by alpha spectrometry for three water samples and four solid samples utilizing two separate preparation and chemical separation methods. Each sample had been previously analyzed as a blind Performance Evaluation (PE) sample, and was chosen for their mixed radionuclide nature and reference activity concentrations. In addition, the solid samples were selected to examine the efficacy of each chemical separation technique in not only releasing the radioactive nuclides from within the matrix, but also removing the non-radioactive constituents during the preparation process.

Science Applications International Corporation (SAIC) and Severn Trent Laboratories (STL) provide nationwide environmental, radiochemical, and mixed waste analytical services for multiple federal and commercial clients. Each St. Louis laboratory location, separately validated by the United States Army Corps of Engineers - Center of Expertise (USACE-CX), maintain

chemical separation facilities as well as full preparation gamma and alpha spectrometry capabilities.

EXPERIMENTAL METHODS

Reference Materials

The three water samples analyzed are former RadChem™ proficiency testing studies created by Environmental Resource Associates. Each sample—RAD-53 Mixed Part A, RAD-53 NaturalS™, and RAD-55 Mixed Part A—is a synthetically prepared drinking water matrix preserved with nitric acid to a pH less than 2.

The four solid samples analyzed are former performance evaluation studies distributed by three organizations as a soil matrix representative of environmental samples. Rocky Flats Soil, prepared by the National Bureau of Standards, contains ^{40}K , ^{90}Sr , ^{137}Cs , ^{241}Am , ^{238}Pu , $^{239/240}\text{Pu}$, the Thorium series, and the Uranium series. The sample contains approximately 55-60% quartz, 25-30% clay, 5-10% alkali feldspars, and 5% plagioclase as possible non-radioactive interferences. Both the diluted Climax Sand Tailings and the diluted Pitchblende Ore were distributed by the United States Environmental Protection Agency, Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (USEPA-EMSL-LV). The Climax Sand Tailings contain quantified amounts of ^{230}Th and ^{226}Ra ; the Pitchblende Ore contains nuclides of the Uranium decay chain. TRM2 contains quantified ^{234}U , ^{238}U , ^{230}Th , ^{226}Ra , and ^{210}Pb , and consists of Uranium Mill Tailings prepared by the Department of Energy (DOE) in Albuquerque, New Mexico. The activity of TRM2 indicates that Uranium in natural abundances had been extracted, leaving levels of the daughter nuclides approximately four times greater than the Uranium concentration.

Concentrated Acid Digestion - Severn Trent Laboratories (STL), St. Louis

Each solid reference material was analyzed in triplicate. The diluted Climax Sand Tailings and diluted Pitchblende ore were aliquot at approximately 0.1 g; the Rocky Flats Soil was aliquot at approximately 1 g. STL analyzed two triplicate sets of the TRM2 reference material at different aliquots, approximately 0.1 g and 0.5 g. Each soil aliquot was dissolved using mixed acid digestion in polypropylene digestion vessels at a temperature of 116-118 °C in a CPI Mod Block™ digestion block. The digestate was twice taken to dryness over a period of 4-5 hours in a mixture of concentrated hydrofluoric, nitric, and hydrochloric acids. Once dry, the digestate was converted to a nitrate form and dissolved in dilute nitric acid and Type II deionized water. Each water sample was aliquot in triplicate except RAD-53 Mixed Part A, which was analyzed in duplicate due to lack of sample volume. RAD-53 Mixed Part A was aliquot at 25 mL, RAD-53 NaturalS™ was aliquot at 100 mL, and RAD-55 Mixed Part A was aliquot at 50 mL. The soil digestates and water samples were precipitated with 0.34 mg barium carrier, 45 mg lead carrier, methyl orange indicator, and 5 mL of 1M citric acid. The samples were traced with 1000 dpm ^{133}Ba tracer and heated to incipient boiling. While stirring, concentrated ammonium hydroxide was added until the yellow endpoint of the indicator was achieved. To ensure precipitate formation, the samples were heated with stirring while adding 2 mL concentrated sulfuric acid and 5 mL of a 200 mg/mL ammonium sulfate solution. After precipitation, the samples were removed from heat and allowed to cool. The supernatant was decanted, and the precipitate transferred to a 50 mL conical centrifuge tube. The precipitate was then washed with both concentrated nitric acid and Type II deionized water with centrifugation after each wash. Basic ethylenediaminetetraacetic (EDTA) reagent was added to the centrifuge tube and heated in

a hot water bath at 80 °C to dissolve the precipitate. After cooling, a lead sulfide precipitation was performed by adding 0.3 mL of a 2% ammonium sulfide solution and 0.5 mL of concentrated sodium hydroxide. The resulting black precipitate was removed through centrifugation. These steps were repeated until a lead sulfide precipitation no longer appeared. At this stage, 1 mL of 1.5 mg/mL lead carrier was added with a few drops of concentrated sodium hydroxide and an additional 0.3 mL of the 2% ammonium sulfide solution; again, if any precipitation occurred, the precipitate was centrifuged and discarded. The supernatant was transferred to a 20 mL luer lock syringe with 0.45 µm syringe filter attached, and filtered into a clean centrifuge tube. Barium sulfate was precipitated by adding 2 mL of a 200 mg/mL ammonium sulfate solution and 3 mL of glacial acetic acid. The samples were heated to 80 °C for five minutes in a hot water bath, and allowed to cool. Each sample was filtered and rinsed with Type II deionized water through filter funnels onto co-precipitation filters. The filters were removed, dried under a heat lamp, and mounted on plastic 1.25" self-adhesive disks. The filters were stored in small Petri dishes and submitted for determination of the ^{133}Ba yield by gamma spectrometry and ^{226}Ra activity by alpha spectrometry.

Pyrosulfate fusion by the Sill Method^{1,2,3,4} - Science Applications International Corporation (SAIC), St. Louis

Sample aliquots, approximately 0.25 g for soil and 30 mL for aqueous samples, were traced with ^{133}Ba and placed in platinum crucibles for digestion. SAIC analyzed two triplicate sets of the Rocky Flats Soil, each at approximately 0.25 g. RAD-53 Mixed Part A was diluted from 76 mL to 100 mL by graduated cylinder in order to achieve the sample aliquot of 30 mL for triplicate analysis. The sample aliquots and a potassium fluoride flux—consisting of potassium fluoride, potassium hydrogen fluoride, and potassium nitrate—were melted on a Meeker™ Blast Burner, resulting in a translucent liquid. Once the solution cooled and formed a crystalline cake, the samples underwent pyrosulfate fusion using sulfuric acid and sodium sulfate, again heated on the Meeker™ Blast Burner. While the samples were cooling, 50 mL deionized water and 1 mL hydrochloric acid were added to 125 mL Erlenmeyer flasks and brought to a boil. The sulfate cake was then transferred to the dilute hydrochloric solution and quickly dissolved. The samples were slowly evaporated to approximately 30 mL, transferred to 50 mL conical centrifuge tubes and cooled to room temperature. Lead nitrate was added to precipitate any sulfates; the samples were centrifuged at high speed for five minutes and the supernatant discarded. The precipitate was washed with 10 mL of a 5% sodium sulfate solution, vortexed, and centrifuged for five minutes. Repeated 10 mL deionized water washes were performed, followed by centrifugation, until the wash was pH neutral. The precipitate was dissolved in alkaline diethylenetriaminepentaacetic acid (DTPA) and filtered through 0.45 µm polypropylene syringe filters that had been previously rinsed with a 20% sodium sulfate solution. A 0.75% barium carrier was added to the samples and mixed. Final precipitation of barium sulfate was performed by the simultaneous additions of 50% acetic acid solution and a barium seeding suspension. The barium seeding suspension consists of barium chloride and sodium sulfate dissolved in sulfuric acid and suspended in deionized water. After the samples had cooled for 20 minutes in a cold-water bath, they were filtered with deionized water through 0.1 µm polypropylene filters that had been conditioned with 70% isopropyl alcohol and approximately 5 mL of a carbon substrate. The filters were dried at room temperature and submitted for determination of the ^{133}Ba yield by gamma spectrometry and ^{226}Ra activity by alpha spectrometry.

RESULTS

Concentrated Acid Digestion - Severn Trent Laboratories (STL), St. Louis

STL's preparation method of concentrated acid digestion produced a mean ²²⁶Ra activity accuracy of 98.9% with a mean ¹³³Ba chemical recovery of 59.8% for the soil matrix samples (see Table I). The accuracy of the soil process was tested by computing the normalized absolute difference (NAD) between the average activities of the TRM2 sample and its duplicate. A value less than 1.96 is considered indicative of effective duplication; the NAD for TRM2 was 0.89. The water matrix samples have a mean ²²⁶Ra activity accuracy of 90.6% with a mean ¹³³Ba chemical recovery of 72.3% (see Table II). Statistically, the samples demonstrate exceptional precision using the mean relative percent difference (RPD) and mean relative standard deviation (RSD) to compare observed activities with the reference activity. The soil matrix samples have a mean RPD of 12.8% and a mean RSD of 15.5%. The water matrix samples have a mean RPD from the reference activity of 13.3% and a mean RSD of 8.6%.

Table I. STL ²²⁶Ra Sample Results – Soil Matrix

Sample ID	Aliquot (L)	Activity ± 2 σ (Bq/L)	¹³³ Ba % Recovery	²²⁶ Ra % Recovery	
RAD-53 Mixed Part A <i>Reference Activity:</i> 9.768 ± 1.717 Bq/L	A	0.025	9.183 ± 0.8099	74.7	94
	B	0.025	8.643 ± 0.9457	53.5	88
	RAD-53 Mixed Part A Means:		8.913 ± 0.8778	64.1	91
RAD-55 Mixed Part A <i>Reference Activity:</i> 9.531 ± 1.658 Bq/L	A	0.05	9.738 ± 0.6682	70.4	102
	B	0.05	10.47 ± 0.6627	76.9	110
	RAD-55 Mixed Part A Means:		9.433 ± 0.6202	74.4	99
RAD-55 NaturalS™ <i>Reference Activity:</i> 10.54 ± 1.835 Bq/L	A	0.1	8.702 ± 0.4166	72.0	83
	B	0.1	9.294 ± 0.4200	81.2	88
	RAD-55 NaturalS™ Means:		8.629 ± 0.4023	75.7	82

Table II. STL ²²⁶Ra Sample Results – Water Matrix

Sample ID	Aliquot (g)	Activity $\pm 2 \sigma$ (Bq/g)	^{133}Ba % Recovery	^{226}Ra % Recovery	
Rocky Flats Soil <i>Reference Activity:</i> 0.0429 \pm 0.0063 Bq/g	A	1.1711	0.0458 \pm 0.0099	68.3	107
	B	1.0047	0.0376 \pm 0.0094	59.7	88
	C	0.9528	0.0411 \pm 0.0125	51.5	96
Rocky Flats Soil Mean:			0.0415 \pm 0.0106	59.8	97
Climax Sand Tailings <i>Reference Activity:</i> 1.68 \pm 0.252 Bq/g	A	0.0975	1.78 \pm 0.228	62.6	106
	B	0.0782	1.94 \pm 0.292	55.9	115
	C	0.1268	1.68 \pm 0.200	53.6	100
Climax Sand Tailings Mean:			1.80 \pm 0.240	57.4	107
Pitchblende Ore <i>Reference Activity:</i> 9.361 \pm 1.591 Bq/g	A	0.1076	12.23 \pm 0.6046	60.8	131
	B	0.0991	7.948 \pm 0.4603	62.3	85
	C	0.0889	8.773 \pm 0.5254	54.5	94
Pitchblende Ore Mean:			9.650 \pm 0.5301	59.2	103
TRM2 <i>Reference Activity:</i> 0.940 \pm 0.033 Bq/g	A	0.5665	0.993 \pm 0.071	62.3	106
	B	0.8006	0.699 \pm 0.048	55.9	74
	C	0.6603	0.728 \pm 0.053	69.7	77
TRM2 Mean:			0.807 \pm 0.057	62.6	86
TRM2 – duplicate <i>Reference Activity:</i> 0.940 \pm 0.033 Bq/g	A	0.1362	0.781 \pm 0.116	63.1	83
	B	0.0722	0.981 \pm 0.169	72.7	104
	C	0.1360	1.10 \pm 0.181	44.6	117
TRM2 – duplicate Mean:			0.954 \pm 0.155	60.1	101

Pyrosulfate fusion by the Sill Method^{1,2,3,4} - Science Applications International Corporation (SAIC), St. Louis

SAIC's preparation of pyrosulfate fusion by the Sill Method produced a mean ^{226}Ra activity accuracy of 111.5% with a mean ^{133}Ba chemical recovery of 85.7% for the soil matrix samples (see Table III). The NAD value calculated for the Rocky Flats Soil sample and its duplicate was 0.34, below the threshold of 1.96. The water matrix samples have a mean ^{226}Ra activity accuracy of 104.7% with a mean ^{133}Ba chemical recovery of 81.9% (see Table IV). The SAIC

preparation method also demonstrates precise values compared to the reference activity of each sample analyzed. The soil matrix samples have a mean RPD of 10.5% with a mean RSD of 11.3%. The water matrix samples have a mean RPD from the reference activity of 6.8% with a mean RSD of 6.6%.

Table III. SAIC ²²⁶Ra Sample Results – Soil Matrix

Sample ID		Aliquot (g)	Activity ± 2 σ (Bq/g)	¹³³ Ba % Recovery	²²⁶ Ra % Recovery
Rocky Flats Soil <i>Reference Activity:</i> 0.0429 ± 0.0063 Bq/g	A	0.2498	0.0489 ± 0.0194	93.1	114
	B	0.2554	0.0401 ± 0.0189	90.8	107
	C	0.2545	0.0774 ± 0.0261	89.8	180
<i>Rocky Flats Soil Means:</i>			0.0555 ± 0.0215	91.2	134
Rocky Flats Soil – duplicate <i>Reference Activity:</i> 0.0429 ± 0.0063	A	0.2572	0.0447 ± 0.0190	88.0	104
	B	0.2502	0.0439 ± 0.0196	89.2	102
	C	0.2541	0.0482 ± 0.0208	88.4	112
<i>Rocky Flats Soil – duplicate Means:</i>			0.0456 ± 0.0198	88.5	106
Climax Sand Tailings <i>Reference Activity:</i> 1.68 ± 0.252 Bq/g	A	0.2507	1.90 ± 0.171	77.7	113
	B	0.2509	2.05 ± 0.185	79.1	122
	C	0.2522	1.78 ± 0.162	84.0	106
<i>Climax Sand Tailings Means:</i>			1.91 ± 0.173	80.3	114
Pitchblende Ore <i>Reference Activity:</i> 9.361 ± 1.591 Bq/g	A	0.2523	9.849 ± 0.6294	89.2	105
	B	0.2500	9.579 ± 0.6138	94.3	102
	C	0.2502	8.954 ± 0.5735	99.0	96
<i>Pitchblende Ore Means:</i>			9.461 ± 0.6056	94.2	101
TRM2 <i>Reference Activity:</i> 0.940 ± 0.033 Bq/g	A	0.2556	0.933 ± 0.110	69.6	99
	B	0.2597	0.971 ± 0.106	85.1	103
	C	0.2499	1.02 ± 0.118	67.8	108
<i>TRM2 Means:</i>			0.975 ± 0.111	74.2	103

Table IV. SAIC ²²⁶Ra Sample Results – Water Matrix

Sample ID	Aliquot (L)	Activity $\pm 2 \sigma$ (Bq/L)	^{133}Ba % Recovery	^{226}Ra % Recovery	
RAD-53 Mixed Part A (diluted) <i>Reference Activity:</i> 7.437 \pm 1.305 Bq/L	A	0.03	6.693 \pm 0.6238	86.3	90
	B	0.03	7.707 \pm 0.6856	82.6	103
	C	0.03	7.404 \pm 0.6660	84.5	100
	<i>RAD-53 Mixed Part A (diluted) Means:</i>		7.268 \pm 0.658	84.5	98
RAD-55 Mixed Part A <i>Reference Activity:</i> 9.531 \pm 1.658 Bq/L	A	0.03	9.934 \pm 0.8025	89.3	104
	B	0.03	10.41 \pm 0.8721	77.6	109
	C	0.03	11.17 \pm 0.9095	88.2	117
	<i>RAD-55 Mixed Part A Means:</i>		10.50 \pm 0.8614	85.0	110
RAD-55 NaturalSTM <i>Reference Activity:</i> 10.54 \pm 1.835 Bq/L	A	0.03	10.63 \pm 0.8691	81.7	101
	B	0.03	12.04 \pm 0.9639	74.6	114
	C	0.03	10.96 \pm 0.9420	72.2	104
	<i>RAD-55 NaturalSTM Means:</i>		11.21 \pm 0.9250	76.2	106

CONCLUSIONS

In order to provide clients and projects with the rapid results necessary for restoration decisions, without sacrificing sensitivity or quality, two independent environmental laboratories compared two preparation and chemical separation methods for analysis of ^{226}Ra in water and soil matrices. Severn Trent Laboratories (STL) in St. Louis, Missouri utilized a method of concentrated acid digestion and multiple precipitations to prepare samples for ^{226}Ra analysis by alpha spectrometry. Science Applications International Corporation (SAIC) in St. Louis, Missouri, in contrast, prepared samples for alpha spectrometry analysis using the methods developed by Claude and David Sill of complete sample digestion through pyrosulfate fusion^{1,2,3,4}. Each technique has been proven to be a reliable method in the past via multiple quality control measures; the evaluation of each method by independent laboratories provided reproducible results that were within, on average, 12% of the expected values of the reference sample activities in both soil and water matrices. The results of this study show conclusively that a modification of the current method for ^{226}Ra activity determination to allow analysis by alpha spectrometry by either sample preparation and chemical separation method will in no way impact the quality of the analytical results. Neither method had a deleterious impact on the ability of the analyzing laboratory to determine chemical yield through the use of a ^{133}Ba tracer. Each process isolated the ^{133}Ba and ^{226}Ra efficiently, yielding average chemical recoveries for each method well within industry-accepted standards.

Future research will concentrate on increased consistency between duplicated samples, improved spectral resolution, and tests to indicate whether matrix interference becomes a greater issue using aliquots of larger than 1 g. Larger soil volumes, as well as more complex soil matrices, may require additional reagents to accurately ensure complete digestion. The potential of sequential counting of ^{226}Ra by alpha spectrometry followed by ^{228}Ra by gas-flow proportional counting will also be examined. Further development will, in addition, focus on combining the methods and seeking industry-wide acceptance as a suitable and effective alternative to ^{226}Ra analysis by the emanation technique⁵. Including receiving, drying and initial preparation, chemical separation, and counting time, these techniques will enable environmental laboratories to complete accurate ^{226}Ra analysis within 48 hours for water samples and 72 hours for soil samples. As a result, the previous timeframe of 21-28 days by EPA Method 903.1⁵ for reporting comprehensive analytical results for ^{226}Ra activity can be significantly reduced to a mere 7-10 days. This comparison study further confirms scientific confidence in, and the benefits of, each preparation and chemical separation procedure.

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