Rapid Method for the Determination of Ra-226 in Hydraulic Fracturing Wastewater Samples

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ABSTRACT

A new method that rapidly preconcentrates and measures ^{226}Ra from hydraulic fracturing wastewater samples was developed in the Savannah River Environmental Laboratory. The method improves the quality of ^{226}Ra measurements using gamma spectrometry by providing up to 100x preconcentration of ^{226}Ra from this difficult sample matrix, which contains very high levels of calcium, barium, strontium, magnesium and sodium. The high chemical yield, typically 80-90%, facilitates a low detection limit, important for lower level samples, and indicates method ruggedness. Ba-133 tracer is used to determine chemical yield and correct for geometry-related counting issues. The ^{226}Ra sample preparation takes < 2 hours.

Introduction

Rapid, effective measurement of Ra-226 (1600 year half-life), the major radioactive component of associated "flowback" and "produced" wastewater, is essential to facilitate regulatory safety decision-making and address public concerns. The sample matrix, which has very high levels of alkaline earth metals (up to 20 g L^{-1}Ca, 10 g L^{-1} Ba, 7 g L^{-1} Sr) is very difficult to process in the laboratory. Nelson et al. reported significant problems regarding ^{226}Ra preconcentration and ^{235}U removal from hydraulic fracturing wastewater samples. [1] This included very low chemical yields, sample processing problems associated with high levels of dissolved solids and precipitation during direct gamma spectrometry measurements. The addition of agar with heating was required to counter the precipitation of ultrafine particulate matter, and a

detection limit of about 3 BqL^{-1} was achieved.

Zhang et al. reported a new ICP-MS method for [226]Ra in hydraulic fracturing wastewater samples with an MDA of 3.7 BqL^{-1}. The authors emphasize the need for a rapid, robust analytical method for NORM (Naturally Occurring Radioactive Material) and [226]Ra, in particular, to advance the understanding of the fate of NORM and to develop best practices for the unconventional gas industry. A column separation, using a Sr/Ba specific resin was needed to remove isobaric interferences, such as the combined mass of Ba plus Sr, which are typically present at high levels. The authors reported that residual Ba was observed in some of the purified samples. This should not be surprising, since high levels of Ba and Sr can easily exceed the capacity of the resin. It should also be noted that in this work no chemical yield tracer was used. [2] When difficult sample matrices are analyzed, use of a chemical yield tracer is important to monitor method performance and ruggedness.

A new method that rapidly preconcentrates [226]Ra from hydraulic fracturing wastewater samples was developed in the Savannah River Environmental Laboratory to improve the quality of [226]Ra measurements. The method provides a lower detection limit and eliminates potential [235]U interference at the 186 keV gamma ray energy used to measure [226]Ra by gamma spectrometry. The rapid method provides up to 100x preconcentration of [226]Ra from this difficult sample matrix, which contains very high levels of calcium, barium, strontium, magnesium and sodium. This new method allows rapid collection of [226]Ra along with the large amounts of barium present in an easily measured, evenly deposited solid layer. Adjustments are made for [226]Ra gamma ray attenuation at 186 keV due to varying levels of solids (primarily BaSO$_4$) in the final sample geometry using the [133]Ba gamma rays at 81 keV and 356 keV. Using this simple, yet effective approach, no drying and weighing to develop a mass attenuation curve for [226]Ra /[133]Ba is needed.

The new method employs a novel precipitation step using calcium fluoride to first remove large amounts of calcium and strontium present, as well as [235]U. This takes advantage of the significant difference in the relative solubilities of calcium fluoride and barium/radium fluoride (k_{sp} BaF$_2$ = 1E-6 mol^{3}L^{-3}, k_{sp} CaF$_2$ = 5.3E-9 mol^{3}L^{-3}). [3] Almost all of the Ba and Ra ions stay in solution, while much of the Ca and U are removed. Ba-133 tracer is used to determine chemical yield, which is typically 80-90%. The high chemical yield facilitates a low detection limit and indicates method ruggedness.

1. **Experimental**

2.1 Reagents

Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS (American Chemical Society) reagent grade. Radiochemical isotope tracer, [133]Ba, was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to ~ 65 Bq mL^{-1} to enable corrections for chemical yield. [226]Ra was obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to ~ 23 Bq mL^{-1}. Flowback waste simulants were prepared by dissolving metal ion chlorides in water. The total ion content, and Ca/Ba ratio was varied to simulate the compositions of flowback water typically encountered.[4]

2.2 Procedures

Sample Preparation for [226]Ra. Figure 1 shows the sample preparation flowchart for the preconcentration of [226]Ra in wastewater samples. Hydraulic fracturing simulant was added to 500 mL centrifuge tubes and acidified by adding 50 mL 12M HCl per 400 mL simulant. Ba-133 tracer was added to each tube, and the samples were mixed well. Calcium fluoride was precipitated by the addition of 20 mL 28M HF and 1 mL 30 wt% H_2O_2 to each tube. The samples were mixed well and centrifuged at 3500 rpm for 10 - 20 minutes, or as needed until the supernate is clear. Removal of calcium, and partial removal of Sr, significantly reduces the volume of the final gamma spectrometry source and eliminates the [235]U interference at the [226]Ra 186 keV gamma emission. Uranium, as U(IV) or U(VI), is effectively removed by the CaF_2 precipitate, with the gL^{-1} levels of calcium. It is critical that uranium be adjusted to U(VI) to facilitate U removal as U(VI) during the subsequent barium sulfate precipitation . Therefore, H_2O_2 is added during the calcium fluoride precipitation so that any residual uranium in the initial supernate will be U(VI). No heating of the sample is required to oxidize uranium to U(VI), as oxidation of uranium ions to U(VI) is very effective at room temperature.

The supernate, which contains about 90% of the Ra/Ba, was transferred to new 500 mL tubes. When smaller aliquots are acceptable, 250 mL tubes can also be used with appropriate scaling of reagents relative to the volume processed. To each supernate, 0.5 mL 30 wt% H_2O_2 was added and mixed well to ensure any remaining uranium is U(VI). Twenty grams of ammonium sulfate were added to each tube. Samples were mixed well to dissolve the $(NH_4)_2SO_4$, and 40 mL ethanol per 400 mL aliquot was added to enhance Ba(Ra) SO_4 precipitation.[5] After waiting 10 to 15 minutes, the tubes were mixed well and centrifuged at 3500 rpm. The supernate was discarded, and the precipitate washed with 50-100 mL water

was added containing 0.2 mL 30 wt% H_2O_2 to remove additional traces of calcium. After mixing well, each tube was centrifuged for 5 minutes at 3500 rpm. The barium sulfate precipitate was transferred to a 50 mL tube (or 250 mL tube if large) using 10-20 mL aliquots of water. At this point, the volume of the precipitate can be noted as a secondary confirmation of the expected gamma attenuation. To each tube, 0.05 mL 30 wt% H_2O_2 was added. Tubes were mixed well and centrifuged 5 minutes. The supernate was discarded and each precipitate was transferred to a 250 mL wide mouth, flat bottom bottle using 10-20 mL aliquots of water. Each 250 mL plastic bottle was centrifuged at 1600-2000 rpm in flat bottom centrifuge bucket to get an evenly deposited layer for gamma spectrometry counting. The sample preparation process takes <2 hours.

If silicates are high in the sample, the sample aliquots may require dilution with water (50% or more) before adding HF to avoid cloudiness in the initial fluoride supernate. To process aliquots larger than 400 mL, aliquots and tracer may be split between multiple tubes to increase total sample aliquot. If samples were split between tubes, the respective barium sulfate precipitates may be recombined in a single tube, and the combined precipitate may be rinsed with water and counted in a single 250 mL bottle. Figures 2 and 3 show how most of the calcium, much of the magnesium and some of the strontium is removed using this fluoride precipitation step. Twenty milliliters of concentrated HF per 400 mL of sample was chosen to limit losses of Ba/Ra, while providing adequate Ca/U removal. The uranium removal is very high because much of the uranium (VI) is co-precipitated with calcium fluoride, and residual U(VI) is effectively removed during subsequent water rinses of the barium sulfate precipitate. The removal of U and Ca is enhanced when the Ca/Ba ratio is ~2, often the case with flowback wastewater samples. However, U/Ca removal is effective over a wide range of sample compositions.

2.3 Gamma Spectrometry

A Canberra (Meriden, CT, USA) high purity germanium detector (Model GC4019), with a relative efficiency of 40% at 1332 keV was used to measure the samples. Canberra Genie 2000 Gamma software (version 1.3) was used to process the samples. A series of barium sulfate precipitate standards containing varying amounts of stable barium, [133]Ba, and [226]Ra were used to establish an efficiency calibration curve.The gamma ray energies and abundances associated with [235]U (185.715keV, 57.0%), [226]Ra (186.211keV, 3.64%) and [133]Ba (80.9979keV, 32.9% and 356.013keV, 62.05%) isotopes were utilized in this method. [6] Figure 4 shows a typical gamma spectrum for the samples and standards. Instead of drying

samples and creating a more traditional mass attenuation calibration curve, the 81 keV gamma ray emission from [133]Ba was used to determine the mass and geometry correction for [226]Ra at 186 keV. Figure 5 shows a plot of the detector efficiency curve for [133]Ba vs [226]Ra, with increasing amounts of barium solids. Hydraulic fracturing wastewater may contain varying levels of barium, resulting in a wide range of potential barium sulfate precipitate volumes (Table 1). Therefore, it is very important to correct for these differences in sample geometry. The [133]Ba gamma ray emission at 356 keV, which typically exhibited minimal attenuation, even for very large barium sulfate precipitates, was used to determine [133]Ba chemical yield. A minor correction to the 356 keV measurement may be applied using the ratio of the [133]Ba 81 keV and 356 keV gamma ray emissions. There are only minor interferences near the 81 keV gamma energy region, and these are insignificant when higher levels of [133]Ba are utilized. Ra-226, Ra-223 and Ra-224, for example, have low abundance gamma rays (0.2% abundance) near 81 keV[6], so relatively high levels of [133]Ba were used to eliminate any significant impact on the 81keV efficiency corrections. The [133]Ba tracer added was ~65 Bq, but this amount could likely be reduced and optimized depending on the levels of [226]Ra typically observed.

2.   Results and Discussion

The simulant wastewater matrix tested consisted of the elements as shown in Table 1. Variations in simulant content were also tested to account for the wide range of alkali metal and alkaline earth metal ion concentrations potentially encountered in flowback waters. Table 2 shows the individual results for the determination of [226]Ra in hydraulic fracturing simulant samples. A wide range of [226]Ra levels were tested. The average [133]Ba tracer recovery was 83.4%, with 1SD of 6.71%, for a wide range of sample aliquots. The measurement uncertainties (k=1 combined standard uncertainty) vary from approximately 5% to 10% of the measured values, with the lowest uncertainties of course with the higher level samples. Several factors affect measurement uncertainty for this method. The uncertainty in the measurement of the [226]Ra gamma ray at 186 keV, the [133]Ba gamma ray measurements at 81 keV and 356 keV, how well the mass attenuation curve was prepared, must all be considered. The measurement uncertainty of the high level [226]Ra spiked samples was approximately 5-8% (at k=1 combined standard uncertainty, CSU) while it increased as expected to approximately 10% CSU at very low levels. The average bias for this set of results was 4.3%, with 1SD of 12.7%. It is interesting to note that the average bias drops to <1% if the one result (+34% bias), relatively close to the MDA (Minimum Detectable Activity) was not considered. Two of the samples had a

very large amount of [235]U added (51.4 Bq), with no adverse analytical impact observed. In other tests, [226]Ra blanks were analyzed with 51.4 Bq [235]U added, and no [235]U was detected. Based on [235]U removal testing, it appears that >99.9% of [235]U is removed. This provides this method very important ruggedness, so that high quality [226]Ra results can be achieved, without concern regarding [235]U interference. While additional validation data is needed over many different types of actual hydraulic fracturing wastewater types to further validate this approach, this initial work has clearly shown that the major problems typically encountered with these samples, the high levels of calcium , barium and strontium can be dealt with very effectively. The robust nature of the method provides high quality measurements and could help characterize and better understand the fate of [226]Ra in the unconventional drilling industry. High quality measurements are required to ensure that public concerns are addressed and reliable methods are essential to maintain the public trust.

The MDA (Minimum Detectable Activity) for [226]Ra using this method with measurement by gamma spectrometry was calculated according to equations prescribed by Currie: [7]

MDA = [2.71+4.65√B]/ (CT*R*V*Eff***A***0.060)

where   B = Total Background counts, = BKG (rate) * sample count time ; CT = sample count time (min)
 R = Chemical Recovery; V = Sample aliquot **(**g) ; EFF = Detector Efficiency ; A = Isotopic abundance 3.56% ; 0.060 = conversion from dpm to mBq.

The MDA for this method for a 1L sample aliquot is <0.74 Bq L^{-1} for a 1000 minute count using a high purity germanium (40% relative efficiency). This is significantly lower than the 3.7 Bq L^{-1} MDA levels typically reported for direct gamma spectrometry and/or ICP-MS methods. Further decrease in the MDA (~5 x) may be possible using a well-type high purity germanium detector, in place of the end cap detectors used in this work. Shorter count times and smaller sample aliquots may be employed for higher level samples. Up to 1.8 L of fracking simulant has been tested using this method. The sample preparation takes < 2 hours. No time-consuming column chemistry is required. No addition of agar with heating is required to counter the precipitation of ultrafine particulate matter. This method does not rely on the ingrowth of [226]Ra progeny, and therefore can be applied quickly and easily without hold times to facilitate sample throughput. The focus of this work is the assay of [226]Ra in hydraulic fracturing wastewater. But it is likely that [228]Ra (via [228]Ac gamma ray emission) can also be measured successfully by gamma spectrometry using this pre-concentration method.

Application to the Assay of Uranium and Thorium Isotopes

In addition, it should also be noted that U and Th isotopes may also be pre-concentrated from hydraulic fracturing wastewater using an iron/titanium hydroxide precipitation, similar to what has been reported by the laboratory for seawater. [8] U-235 and [228]Th can be collected together using [229]Th as a tracer (88.5 keV, 23.9% abundance) for both U and Th isotopes by gamma spectrometry. If the [229]Th gamma ray (183.9 keV, 0.14% abundance) cannot be resolved from [235]U (185.7 keV, 57% abundance), then U-235 can likely be measured at 143.76 keV (10.96% abundance). Alternately, if the higher abundance U-235 gamma ray at 185.7 keV is desired, U and Th can be further separated from each other using LaF_3 chemistry and assayed separately in small, homogeneous liquid geometries. Additional column chromatography techniques to separate U and Th for the measurement of alpha-emitting isotopes by alpha spectrometry may also be employed. [9] Figure 6 illustrates how U/Th can be preconcentrated from hydraulic fracturing solutions using iron/titanium hydroxide precipitation and measured by gamma spectrometry. If necessary, LaF_3 chemistry can be used to separate uranium and thorium isotopes from each other for gamma spectrometry or, alternately, to collect uranium and thorium for extraction chromatographic separation and alpha spectrometry. [10] Preliminary results using this separation method shows thorium-229 tracer yields of 95.9% ± 5% (1SD), with a U removal of >99.8%. It should be noted that the [229]Th progeny, [225]Ac, will likely interfere with [228]Th assay by gamma spectrometry at 84.4 keV, so measurement of the [228]Th daughter, [224]Ra, is likely needed following sufficient ingrowth (~1.5 days). Based on previous work removing another alkaline earth metal, ^{90}Sr, from its' daughter, ^{90}Y, one would expect the [228]Th/[224]Ra separation time to be at the last water rinse of the Fe/Th hydroxide precipitate. [11]

Further Study

It should also be possible to determine [228]Ra along with [226]Ra by measuring the daughter of [228]Ra, [228]Ac, in the barium sulfate precipitate using gamma spectrometry. Following a sufficient ingrowth period, typically 36 hours or more, one could measure [228]Ac using the 338.3 keV (11.27% abundance) or 911.20 keV (25.8% abundance) gamma rays, with appropriate geometry corrections as well.   It is also likely that ^{210}Pb can be collected with U/Th during the initial hydroxide precipitation, perhaps with Pb carrier added to facilitate chemical yields. The assay of [228]Ra and ^{210}Pb using these new approaches has not yet been tested in our laboratory, but these potential applications definitely warrant further study.

3. Conclusions

A new method that rapidly preconcentrates [226]Ra from hydraulic fracturing wastewater samples was developed to improve the quality of Ra-226 measurements using gamma spectrometry. The method provides a lower detection limit and eliminates potential [235]U interference at the 186 keV gamma ray energy used to measure [226]Ra. The rapid method provides up to 100x preconcentration of [226]Ra from this very difficult sample matrix. This new method allows rapid collection of [226]Ra along with the large amounts of barium present in an easily measured, evenly deposited solid layer, with adjustments made for gamma ray attenuation at 186 keV using the [133]Ba gamma rays at 81 keV and 356 keV.

Acknowledgments

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Table I Typical Hydraulic Fracturing Simulant Matrix

element	g L^{-1}	source	range (g L^{-1}) in typical flowback waters*
Na	44	NaCl	
K	1	KCl	0.008-1.01
Mg	1.8	MgCl$_2$ 6H$_2$O	0.022-1.8
Ca	15	CaCl$_2$ 2H$_2$O	0.204-14.8
Sr	5.4	SrCl$_2$ 6H$_2$O	0.046-5.35
Ba	7	BaCl$_2$ 2H$_2$O	0.076-13.6
Fe	1	FeCl$_3$	0.014-0.059
Si	0.025	Na$_2$SiO$_4$ Solution	

From Reference 3

Table II ^{226}Ra results for Hydraulic Fracturing Simulant Matrix

	simulant aliquot (mL)	U-235 added (51.4 Bq)	count time (min)	Ba-133 yield (%)	Ra-226 added (Bq)	Ra-226 measured (Bq)	Ra-226 measured (Bq L^{-1})	CSU (Bq L^{-1})	Bias (%)
1	200	Yes	960	83.5	0.94	0.95	4.8	0.24	1.6
2	400	No	720	90.3	23.5	23.0	57.5	2.88	-2.0
3	450	No	720	89.1	23.5	22.9	51.0	2.55	-2.3
4	450	No	720	87.3	1.17	1.57	3.5	0.24	34.1
5	450	No	720	86.3	0.74	0.75	1.7	0.17	2.0
6	200	No	960	83.9	0.94	1.03	5.2	0.26	9.8
8	450	No	960	80.6	4.70	4.36	9.7	0.48	-7.1
9	900	No	960	82.0	4.70	4.37	4.9	0.24	-6.9
10	1800	Yes	960	71.2	4.70	5.14	2.9	0.20	9.4
			avg.	83.8					4.3
			SD	5.71					12.7

CSU= combined standard uncertainty

Figure 1 ^{226}Ra Preconcentration from Hydraulic Fracturing Samples

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┌─────────────────────────────────────────────┐
│ Add Ba-133 tracer and 1mL 30 wt% H₂O₂        │
│ to sample aliquot in 250 mL or 500 mL tubes*.│
│ Add 50 mL 12M HCl per 400 mL sample aliquot. │
│ Mix well.                                     │
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│ Add 20 mL 28M HF per 400 mL aliquot to each  │
│ tube. Cap and mix well. Centrifuge 10-20     │
│ minutes at 3000 rpm or more as needed until  │
│ supernate is clear.                           │
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│ Transfer supernate to 250 mL or 500 mL       │
│ centrifuge tube. Add 0.5 mL 30 wt% H₂O₂ and  │
│ mix well. Add 20 g ammonium sulfate to each  │
│ tube. Add ~40 mL ethanol to each tube per    │
│ 400 mL aliquot. Mix well and wait 10 to 15   │
│ minutes. Centrifuge 5 to 10 minutes. **       │
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│ Discard supernate. Add 50-100 mL water, 0.2  │
│ mL 30 wt% H₂O₂, mix well and centrifuge 5    │
│ minutes.                                      │
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│ Discard supernate. Transfer precipitate to   │
│ 50 mL tube (or 250 mL tube if large) using   │
│ 10-20 mL aliquots of water. Add 0.05 mL 30   │
│ wt% H₂O₂, mix well and centrifuge 5 minutes. │
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│ Transfer precipitate to 250 mL wide mouth    │      │ Count by gamma   │
│ plastic bottle using 10-20 mL aliquots of    │ ───▶ │ spectrometry     │
│ water. Centrifuge at 1600-2000 rpm in flat   │      │                  │
│ bottom centrifuge bucket.                     │      └──────────────────┘
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Add Ba-133 tracer and 1mL 30 wt% H_2O_2 to sample aliquot in 250 mL or 500 mL tubes. Add 50 mL 12M HCl per 400 mL sample aliquot. Mix well.*

Add 20 mL 28M HF per 400 mL aliquot to each tube. Cap and mix well. Centrifuge 10-20 minutes at 3000 rpm or more as needed until supernate is clear.

*Transfer supernate to 250 mL or 500 mL centrifuge tube. Add 0.5 mL 30 wt% H_2O_2 and mix well. Add 20 g ammonium sulfate to each tube. Add ~40 mL ethanol to each tube per 400 mL aliquot. Mix well and wait 10 to 15 minutes. Centrifuge 5 to 10 minutes. ***

Discard supernate. Add 50-100 mL water, 0.2 mL 30 wt% H_2O_2, mix well and centrifuge 5 minutes.

Discard supernate. Transfer precipitate to 50 mL tube (or 250 mL tube if large) using 10-20 mL aliquots of water. Add 0.05 mL 30 wt% H_2O_2, mix well and centrifuge 5 minutes.

Transfer precipitate to 250 mL wide mouth plastic bottle using 10-20 mL aliquots of water. Centrifuge at 1600-2000 rpm in flat bottom centrifuge bucket.

Count by gamma spectrometry

* Some sample may need to be diluted with water 50% or more if silicates that cause cloudiness are high. Aliquots and tracer may be split between multiple tubes to increase total sample aliquot.

** If samples were split between tubes, combine the respective barium sulfate precipitates in a single tube then rinse the combined precipitate with water and proceed.

Figure 2. Removal of Sample Matrix Interferences vs HF Added.
Simulant Composition From Table 1.

Figure 3. Removal of Sample Matrix Interferences vs Simulant Dilution.
Simulant Composition From Table 1.

Figure 4 Gamma Spectrometry Sample Spectra

Figure 5   Plot of [226]Ra Efficiency (186 keV) and Ba-133 Efficiency (356 keV) vs. [133]Ba Efficiency (81 keV)

Figure 6   Preconcentration of U/Th Isotopes from Hydraulic Fracturing Samples
for Assay by Gamma or Alpha Spectrometry

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┌─────────────────────────────────────────┐
│ Add Th-229 tracer to sample aliquot in 250 mL │
│ tubes. Add 50 mg Fe and 1mL 20% TiCl per 200 mL │
│ sample aliquot. Mix well. │
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│ Adjust pH to ~8.5 with NH₄OH. Cap and mix well. │
│ Centrifuge 5 minutes at 3000 rpm or more as │
│ needed until supernate is clear. Discard supernate. │
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│ Add 100 mL water (pH 8.7-8.9), mix well. │
│ Centrifuge and discard water rinse to remove Ca. │
│ Repeat once more with 50 mL water rinse. │
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│ Discard water rinse. Add 1 mL 12 HCl to dissolve │
│ small Fe/Ti ppt and transfer to 50 mL tube. Rinse │
│ tube with 5 mL 1M HCl and transfer rinse to 50 mL │
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│ Add 5 mg La, 0.5 ml 30 wt% H₂O₂, 2 mL 28M HF and │
│ mix well. Centrifuge 5 minutes to collect LaF₃ │
│ precipitate. Th⁺⁴ precipitates and U⁺⁶ stays in │
│ solution. Pour off supernate and collect for U-235 by │
│ gamma spectrometry. │
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│ Add 2 mL 1M HCl to La/Th precipitate, 0.2 mL 30 │
│ wt% H₂O₂,.5 mL 28M HF. Mix well. │
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│ Redissolve LaF₃ precipitate with 4 mL 6M HNO₃, 1 │
│ mL 3M HNO₃-0.25M H₃BO₃ and 4 mL 2M Al(NO₃)₃. │
│ Mix well. Sample may be counted by gamma │
│ spectrometry or column extraction applied for assay │
│ by alpha spectrometry. │
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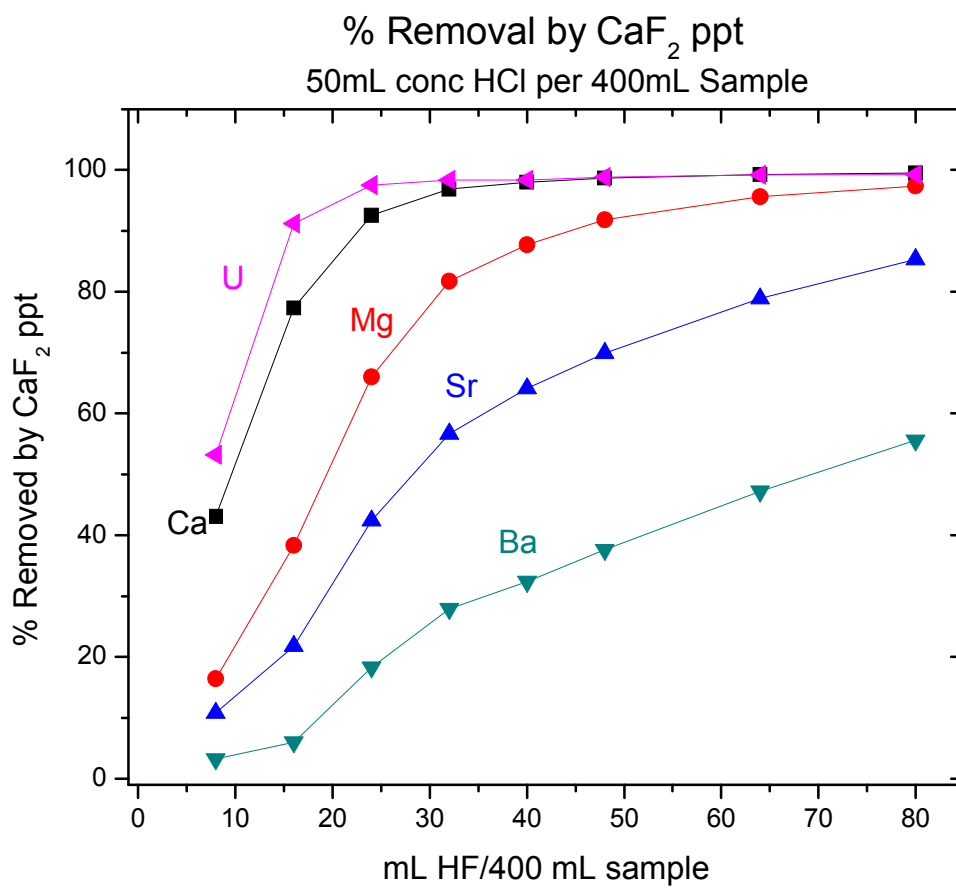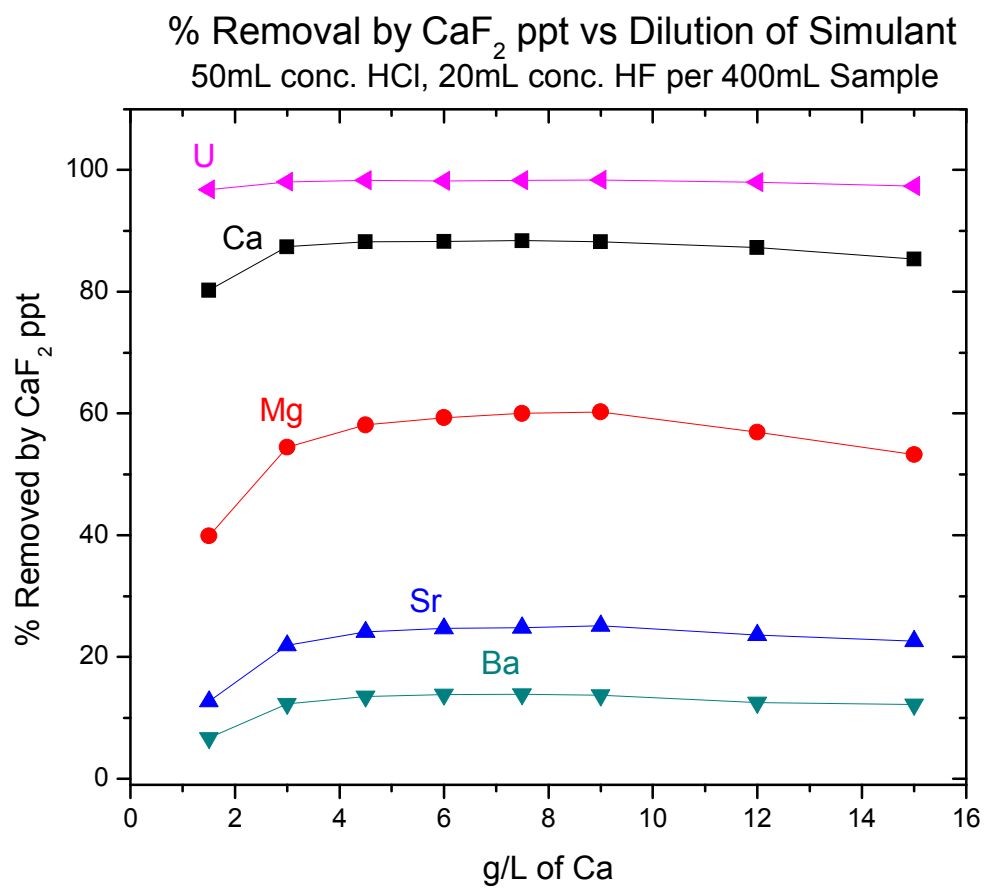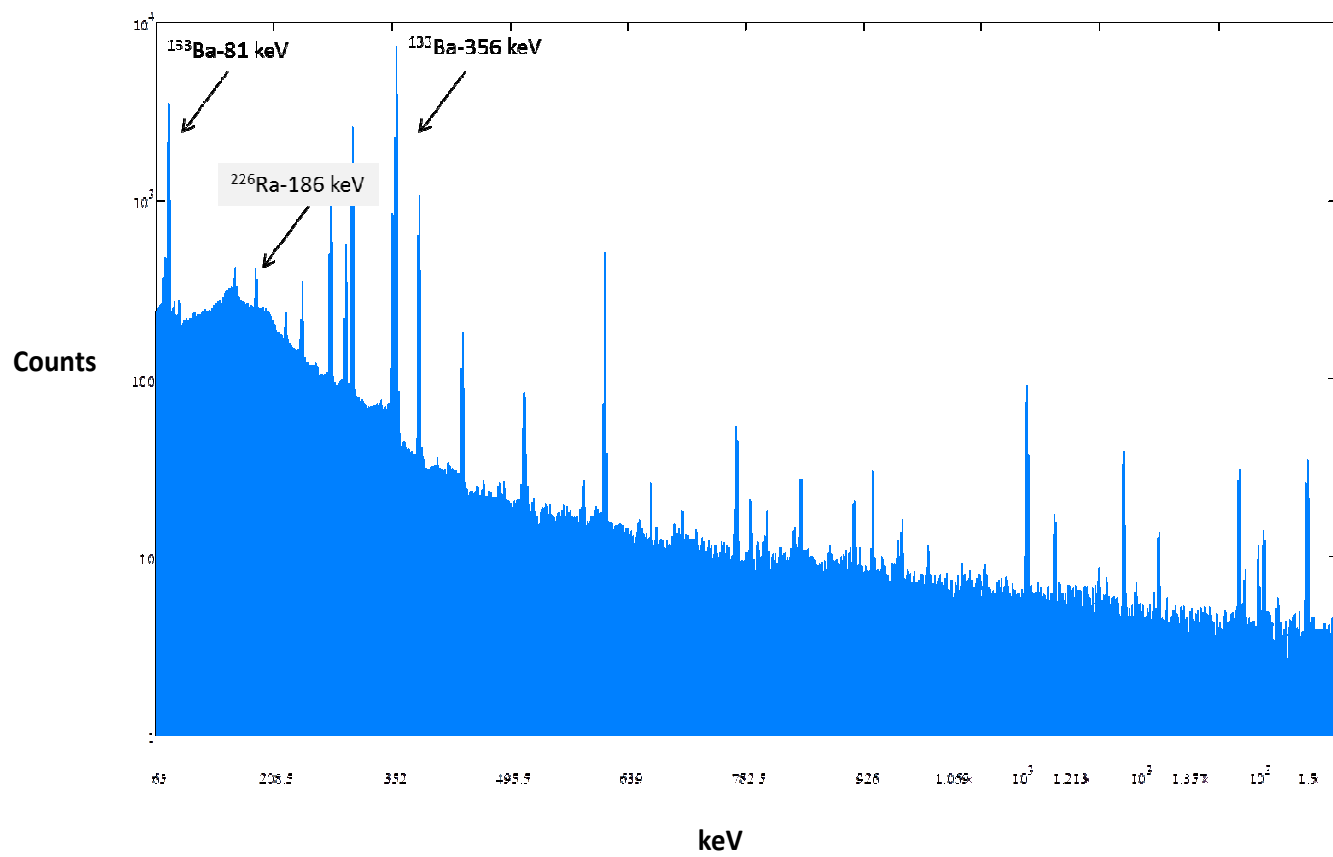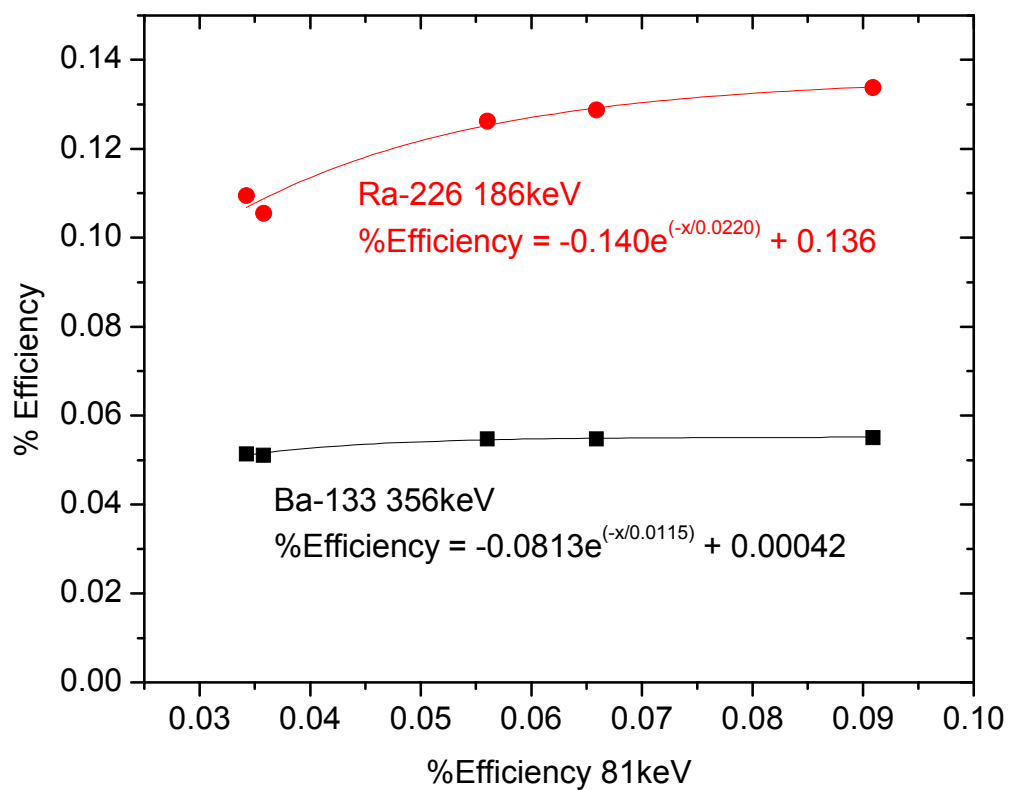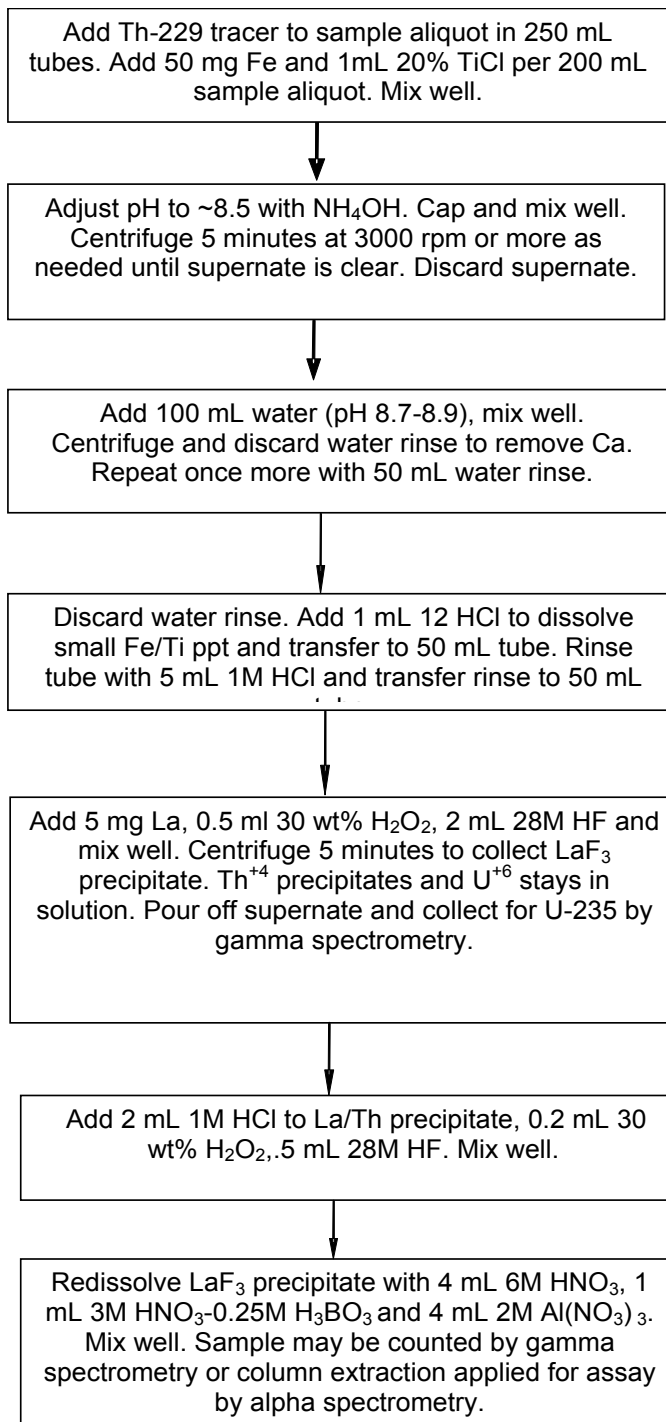
Box 1 — top right (green):

Transfer solution to 20 mL vial and assay using gamma spectrometry to measure U-235 at 185.7 keV or 143.76 keV.

If separation of U/Th is needed so that 185.7 kev may be used, continue with LaF_3 chemistry.

Box 2 — lower right (blue):

U and Th can also be collected with LaF_3 together to remove the Fe and Ti ions if U is reduced to U(IV) using Ti(III).

The LaF_3 precipitate can be dissolved and processed by extraction chromatography and purified for alpha spectrometry assay using TEVA +TRU Resin.