Rapid Determination of ^{226}Ra in Emergency Urine Samples

Sherrod L. Maxwell[1], Brian K. Culligan [1], Jay B. Hutchison[1], Robin C. Utsey[1] and Daniel R. McAlister[2]

Savannah River National Laboratory, Building 735-B, Aiken, SC 29808, USA

[2]PG Research Foundation, Inc. Lisle, IL 60532

Savannah River National Laboratory, Building 735-B, Aiken, SC 29808, USA

[1] Author for correspondence (email: sherrod.maxwell@srs.gov)

phone 803-952-7473

fax 803-952-7881

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Abstract

A new method has been developed at the Savannah River National Laboratory (SRNL) that can be used for the rapid determination of ^{226}Ra in emergency urine samples following a radiological incident. If a radiological dispersive device (RDD) event or a nuclear accident occurs, there will be an urgent need for rapid analyses of radionuclides in urine samples to ensure the safety of the public. Large numbers of urine samples will have to be analyzed very quickly. This new SRNL method was applied to 100 ml urine aliquots, however this method can be applied to smaller or larger sample aliquots as needed. The method was optimized for rapid turnaround times; urine samples may be prepared for counting in <3 hours. A rapid calcium phosphate precipitation method was used to pre-concentrate ^{226}Ra from the urine sample matrix, followed by removal of calcium by cation exchange separation. A stacked elution method using DGA Resin was used to purify the ^{226}Ra during the cation exchange elution step. This approach combines the cation resin elution step with the simultaneous purification of ^{226}Ra with DGA Resin, saving time. ^{133}Ba was used instead of ^{225}Ra as tracer to allow immediate counting; however, ^{225}Ra can still be used as an option. The rapid purification of ^{226}Ra to remove interferences using DGA Resin was compared with a slightly longer Ln Resin approach. A final barium sulfate micro- precipitation step was used with isopropanol present to reduce solubility; producing alpha spectrometry sources with peaks typically <40 keV FWHM (Full Width Half Max) . This new rapid method is fast, has very high tracer yield (>90%), and removes interferences effectively. The sample preparation method can also be adapted to ICP-MS

measurement of ^{226}Ra, with rapid removal of isobaric interferences.

Introduction

^{226}Ra is an alpha emitter, with alpha energies at 4.78 MeV (94.5%) and 4.61 MeV (5.55%). It has a 1600 year half- life and is radiotoxic, following calcium in the food chain into bones. Exposure to high levels of internal contamination by ^{226}Ra can lead to severe, acute or chronic health effects. Rapid methods for environmental and bioassay samples are essential in the aftermath of an emergency radiological event to determine if immediate medical treatment is needed to mitigate acute or long-term health effects. [1]

A rugged method for ^{226}Ra in urine is needed to allow rapid detection in urine samples. The recent theft of nuclear material in Mexico highlights the need for nuclear safeguards and raises concerns about a radiological dispersive device (RDD) or "dirty bomb", again illustrating the need for rapid environmental and bioassay methods. [2] ^{226}Ra has been identified by the International Atomic Energy Agency as a radionuclide that can harm human health if used in a terrorist attack using a RDD. [3] The nuclear accident at Fukushima Daiichi in March, 2011 also points out the continuing need for rapid radiochemical methods following a radiological emergency.

Kehagia et al reported a method for ^{226}Ra in urine that involved evaporation of the sample, wet-ashing, heating overnight in a furnace, precipitation steps and separation using both anion and cation resin. The method took 2 days to prepare 4 samples. Since a lower activity ^{225}Ra (^{217}At) standard was used as a tracer, a 4 day wait time was utilized prior to counting. Chemical yields were 50-70%. [4]

Dai et al reported a new rapid method for ^{226}Ra in urine using ion exchange resin. ^{224}Ra was used as a tracer, added with its parent ^{228}Th. After separation, hydrous titanium oxide precipitation and $BaSO_4$ micro-precipitation were performed. The average chemical yield was ~76%. The method has an MDA (Minimum Detectable Activity) of 0.22 Bq L^{-1} with 4 hour count time and 20 ml of urine sample. [5] The use of ^{224}Ra as a tracer is an interesting option but raises questions about whether any ^{224}Ra could be present in the sample already. In addition, ^{224}Ra, which has a 3.66 day half-life, has a very rapid ingrowth of progeny which are present in the alpha spectrum.

Sadi also reported a new rapid method for ^{226}Ra in urine samples using a dispersive liquid-liquid microextraction technique. ^{226}Ra was measured by liquid scintillation counting, with an MDA of 0.15 Bq L^{-1}, lower than a target sensitivity of 0.2 Bq L^{-1} for ^{226}Ra in urine samples. A single urine sample could be completed in <5 hours and <20 hours for a batch of 6 samples. Each sample was counted in a sequential

manner by liquid scintillation counting for 120 minutes. It appears that no tracer to monitor yield was used for this work, but chemical yields were greater than 90%. [6]

Cozzella et al. [7] reported a method for ^{226} Ra in urine. ^{226}Ra was co-precipitated on MnO_2 from 500-1000 ml aliquots, followed by purification on cation exchange resin, and measurement by quadrupole mass spectrometry. The average chemical yield was 75.8%. The procedure described in this work, including pre-concentration of ^{226}Ra by MnO_2, resin separation and quantification by ICP-MS could be completed in 2 days for a batch of 4 samples. While the final ICP-MS measurements were relatively quick, the overall method was still somewhat time-consuming.

A rapid ^{226}Ra method for environmental samples was reported by this laboratory in 2012 [8]. It used calcium carbonate precipitation, cation exchange removal of calcium and final removal of interferences with Ln Resin (HDEHP extractant-coated resin from Eichrom Technologies, Lisle, IL, USA). The method used ^{225}Ra tracer and the ^{217}At ingrowth occurred during the alpha spectrometry count begun the same day. The count time had to be long enough to allow sufficient ^{217}At ingrowth and tracer counts. The chemical yields were ~92% for water samples. This approach can be applied to urine samples, but a slightly different approach was taken.

A new rapid method to assay ^{226}Ra in emergency urine samples was developed at SRNL that does not use calcium carbonate precipitation or Ln Resin. Instead of calcium carbonate, calcium phosphate was used to collect ^{226}Ra rapidly from the urine sample. Due to its lower solubility, calcium phosphate can be used with less calcium added, while achieving very effective co-precipitation of ^{226}Ra. Less calcium added means less cation resin used, reducing column rinses, elution volumes and overall sample preparation time. It has also been found in this laboratory that the use of large amounts of sodium carbonate can result in slightly higher^{226}Ra blanks (~10-15 counts using 25% efficiency detectors over a 16 hour count time), presumably due to contamination of the sodium carbonate reagent with trace amounts of ^{226}Ra. In contrast, calcium phosphate lowers blanks significantly, very important for the analysis of urine samples. DGA Resin can be used instead of Ln Resin to remove residual Ca, as well as radionuclides such as U, Th, Po, Bi and Pb, at much higher acid concentrations. This eliminates the extra time associated with preparing samples for the Ln Resin separation, where the eluent from the cation resin step has to be evaporated gently on low heat to avoid problems effectively redissolving samples in very low acid. The use of DGA Resin eliminates this concern, as final evaporated eluents are redissolved in much stronger acid.

As in the previous work, a final barium sulfate micro-precipitation step with isopropanol present to

reduce solubility was used yielding alpha spectrometry sources with peaks <40 keV FWHM. This new rapid method is fast, has very high tracer yield (>90-98%), and removes interferences effectively. The method can be used with ^{133} Ba or ^{225}Ra tracer.

^{225}Ra is particularly advantageous as a tracer when there is a possibility of divergence between Ba and Ra during the sample preparation steps, more likely with difficult matrices such as soil. It also allows the removal of native Ba in soil, concrete and brick samples using Sr Resin. The removal of native Ba in the sample in this manner prevents alpha peak resolution problems. Without Ba removal, solid sample sizes are limited and longer count times may be needed.

Ba/Ra divergence does not seem to be an issue using this new method for urine. When the Ra/Ba behavior is nearly identical, the use of ^{133}Ba allows more immediate counting of the samples. In addition, the use of ^{133}Ba allows the simultaneous assay of ^{224}Ra in the alpha spectrum. The progeny of ^{225}Ra interfere with the assay of ^{224}Ra. This method was designed to be fast, allow immediate counting and allow the assay of ^{224}Ra, if desired. The use of a tracer provides corrections for minor losses and offers defensibility for sample analyses used to protect the public.

Based on calculations by Saunders using NCRP 161, the ^{226}Ra clinical decision guide (CDG) target levels for ^{226}Ra for pregnant female and for children are estimated to be at 24 Bq L^{-1} on day 1 and drop to 0.17 Bq L^{-1} by day 20. [1, 9] The CDG levels for pregnant female and children are 1/5 the target levels for other adults. This new method, using a 100 ml aliquot size, can easily provide a detection limit well below these target levels. While 16 hour counts were used in this work, 1-2 hour count times can be used to meet these CDG target levels, even with smaller urine aliquots. This rapid processing of samples will allow large numbers of people to be screened quickly in a radiological emergency.

Experimental

Reagents

The resins employed in this work are Cation Resin (50W-X8, Hydrogen form, 200-400 mesh), Ln-Resin® (bis (2-ethylhexyl) phosphoric acid) and DGA Resin (N,N,N',N'-tetraoctyldiglycolamide), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA). Nitric 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 reagent grade. Radiochemical isotopes ^{226}Ra and ^{133}Ba were obtained

from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq ml^{-1} and 37 Bq ml^{-1} respectively.

Procedures

Column preparation. Cation exchange resin (Eichrom 50WX8, 200-400 mesh) was obtained as bulk resin and columns were prepared by weighing out the resin amounts in large ion exchange column reservoirs. (Environmental Express, Mount Pleasant, SC, USA). Ln Resin and DGA Resin cartridges containing 2 ml of each resin were obtained from Eichrom Technologies, Inc. (Lisle, IL). Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies) that will handle 24 samples at a time. Flow rates of 1-2 ml min^{-1} were typically used. The cation resin with 200-400 mesh was used with optimum flow rates using (in most cases) gravity flow. If a larger pore size cation resin is used, for example, 100-200 mesh allowing higher flow rates, slightly more resin may be needed to maintain >90% chemical yields.

Apparatus. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box. A large volume vacuum box liner was used to collect rinses to eliminate having to change out 50 ml tubes during the load and rinse steps.

Sample Preparation. Figure 1 shows the sample preparation method that was used. Urine sample aliquots of 100 ml were acidified to ~pH 2 in 225 ml centrifuge tubes using nitric acid. To each replicate aliquot, ~1000 pCi (37 Bq) of ^{133}Ba tracer to determine chemical yield. The 100 ml urine aliquots were spiked with known amounts of ^{226}Ra. A set of blank urine samples were also analyzed.

To concentrate the Ra rapidly and remove potentially interfering matrix constituents from each urine sample, 50mg Ca and 5 ml 3.2M $(NH_4)_2\ HPO_4$ were added. The pH was adjusted to ~pH 10 with 14.5M NH_4OH using phenolphthalein indicator. A pH meter can be used for dark urine samples, if needed. Each sample was mixed well, allowed to sit ~5 minutes and centrifuged at ~3500 rpm for ~6 minutes. The supernatant was discarded and the calcium phosphate precipitate was dissolved in 10 ml of 1.5 M HCl, and transferred to a 50 ml centrifuge tube. The 225ml tube was rinsed well with 7 ml of 1.5 M HCl and this rinse solution was added to each dissolved sample. This method can easily be adapted to a smaller sample aliquot in 50 ml tubes with less Ca, when less urin is available.

The precipitate was dissolved directly into the load solutions for further processing, with minimal

organics present that could be seen just at the top of the cation resin column. As an option, the calcium phosphate precipitate can be wet-ashed on a hot plate with 15.8M HNO_3 and 30wt% H_2O_2 added to destroy any residual organics, and then dissolved into the column load solution. The precipitate can also be dissolved and loaded directly from the 225ml tubes to save time.

Column separation. Figure 2 shows the column separation used that employs cation resin with a stacked elution of ^{226}Ra through DGA Resin to remove interferences simultaneously with the elution step. The cation resin column contained 3 grams of cation resin (200-400 mesh), although slightly more resin can be used for larger sample aliquots containing large amounts of Ca. The columns were set-up on a vacuum box with a large inner liner to collect rinses, however, vacuum is normally only needed to get the flow started.

Prior to loading the sample, the cation resin was cleaned as follows to ensure very low blanks. After rinsing with water, 20 ml 6M HCL was passed through the cation resin at~3-4 drops sec^{-1}, followed by water and then 10ml 0.5M HCl. The samples were loaded at ~1 drop sec^{-1}. After sample loading, the column was rinsed at ~1-2 drops/second with 15ml 3M HCl to remove Ca. This step also removes Pb, Bi and U ions that may be present in the sample.

After Ca removal, a 2ml DGA cartridge was placed onto the bottom of each cation column, with a new labeled tube below each column to collect the purified eluent. To elute Ra from each cation column, 20 ml 5M HNO_3 was added to each column at ~1 drop sec^{-1}. The cation resin column was then removed and an additional 5ml 5M HNO_3 was added to each DGA cartridge to rinse. The eluents were transferred to 250 ml glass beakers and evaporated to dryness quickly on a hot plate, with 3 ml 30wt% H_2O_2 of tube rinse added to each beaker. Each sample was taken to dryness quickly. The samples were redissolved in 10 ml 1.5M HCl with heating on a hot plate, transferred to a 50 ml tube, and then the beakers were rinses with two 5 to7ml volumes of 1.5M HCl to give ~20ml 1.5M HCl total. The purified samples were ready for final microprecipitation.

Three grams of ammonium sulfate were added to each tube and mixed well to dissolve completely. Fifty micrograms of barium were added to each solution and mixed well. Five milliliters isopropanol were added to each tube and mixed again. The tubes were iced for 15 minutes, periodically vortexed during that time (beginning, middle and on removal from ice). The solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve- Filter-Eichrom Technologies), rinsing the filters with 20% isopropanol. The filters were dried under a heat lamp, counted by gamma spectrometry to determine ^{133}Ba yield and alpha

spectrometry to measure ^{226}Ra. It should be noted that sulfuric acid may be used instead of ammonium sulfate, if desired. The disposable Resolve Filters funnel units were used on vacuum boxes with a liner to save time.

Figure 3 illustrates how Ca is retained on DGA Resin with the 5M HNO_3 eluent used. While most of the Ca present is removed using the cation resin step, a small residual amount of Ca may remain and is removed on DGA Resin. This ensures that Ca does not interfere with the barium sulfate microprecipitation step and adversely affect alpha peak resolution.

Figure 4 shows the behavior of Ba and Ra on Cation Resin under the method conditions used to test Ba/Ra divergence. It was observed that <0.6% ^{133}Ba was lost in the 3M HCl rinse step. ^{133}Ba was received from Eckert and Ziegler Isotope Products. ^{223}Ra was milked from ^{227}Ac as previously described. [10] Samples containing ^{133}Ba (356.01 keV) and ^{223}Ra (269.46 keV) in polypropylene gamma tubes (Perkin Elmer) were counted for 500 seconds on an ORTEC GEM15-70 high purity germanium coaxial detector system. Gamma activities for ^{133}Ba and ^{223}Ra were determined using the Gamma Vision version 6.09 software (ORTEC, Oak Ridge, TN, USA). [10]

The calcium phosphate approach was also tested with Ln Resin as well as DGA Resin to compare methods. The Ln Resin method was performed as described below. After elution of Ra from the cation resin with 8M HNO_3, the samples were evaporated to dryness, being careful to heat gently near dryness to avoid redissolution problems. The samples were redissolved in 2 ml 0.1M HCl, warmed on a hot plate, diluted with 8ml water, and reheated briefly. After cooling, the samples were passed through Ln Resin to remove interferences, rinsing Ln resin with 10 ml 0.02M HCL. The 0.02M acidity was set to ensure Ra was eluted and any residual Ca was retained. To each final purified solution containing 20 ml 0.02M HCl, 3 ml 12M HCl was added to increase the acidity to ~1.5M HCl.

Results and Discussion

Table 1 shows the measured values for the determination of ^{226}Ra in a set of eight 100 ml urine samples using calcium phosphate and Ln Resin. Each 100 ml urine sample was spiked with 73.67 mBq. ^{133}Ba in the final sample test source (25 mm filter) was measured using a high purity germanium detector for 15 minutes each. The average ^{133}Ba tracer yield was 96.3% ± 3.6% at 1SD (standard deviation), and ^{226}Ra results were corrected for the ^{133}Ba tracer yields. The average measured value for ^{226}Ra was 71.5 mBq smp^{-1} (715 mBq L^{-1}) and the average bias for the eight ^{226}Ra measurements was -2.9%, with 1SD of 1.7 mBq smp^{-1}. The term “smp” is used here to mean the 100 ml sample aliquot analyzed. The results were excellent, but the Ln

Resin approach did require a bit more attention and care during the evaporation steps to avoid baking the samples. Loading very low acid (0.02M HCl) to Ln Resin also seemed to result in varying flow rates.

Table 2 shows the measured values for the determination of ^{226}Ra in a set of six 100 ml urine samples using the Cation + DGA Resin stacked elution option. Each 100 ml urine sample was spiked with 73.67 mBq. ^{133}Ba was measured in the final sample test source using a high purity germanium detector for 15 minutes each. The average ^{133}Ba tracer yield was 92.8% ± 3.0% at 1SD, and ^{226}Ra results were corrected for the ^{133}Ba tracer yields. The average measured value for ^{226}Ra was 76.5 mBq smp^{-1} (765 mBq L^{-1}) and the average bias for the six ^{226}Ra measurements was 3.9%, with 1 SD of 4.7 mBq smp^{-1}.

Table 3 shows the measured values for the determination of ^{226}Ra in a set of six more 100 ml urine samples using the Cation + DGA Resin stacked elution option. Each 100 ml urine sample was spiked with 18.42 mBq. ^{133}Ba was measured in the final sample test source using a high purity germanium detector for 15 minutes each. The average ^{133}Ba tracer yield was 92.8% ± 3.0% at 1SD, and ^{226}Ra results were corrected for the ^{133}Ba tracer yields. The average measured value for ^{226}Ra was 18.4 mBq smp^{-1} (184 mBq L^{-1}) and the average bias for the eight ^{226}Ra measurements was -2.7%, with 1SD of 0.8 mBq smp^{-1}.

Table 4 shows the measured values for the determination of ^{226}Ra in a set of six 100 ml blank urine samples using the Cation + DGA Resin stacked elution option. To each of the blank urine samples, 74 mBq ^{210}Po and 74 mBq ^{238}U were added to test for removal of these two potential interferences. ^{133}Ba was measured in the final sample test source using a high purity germanium detector for 15 minutes each. The average ^{133}Ba tracer yield was 92.4% ± 4.7% at 1SD, and ^{226}Ra results were corrected for the ^{133}Ba tracer yields. The average measured value for ^{226}Ra in the blank urine was 0.146 mBq smp^{-1} (1.46 mBq L^{-1}) with 1 SD of 0.122 mBq smp^{-1}. Based on the consistently low blank ^{226}Ra measurements versus MDA levels, the ^{210}Po and ^{238}U were effectively removed and the blank levels were very low. This is a significant improvement over ^{226}Ra blanks when sodium carbonate is added. For example, ^{226}Ra blank levels with calcium carbonate (25 ml 2M sodium carbonate is used with 150 mg Ca) , blanks levels of ~1.5 mBq smp^{-1} are not unusual. Reducing the sodium carbonate added is an option to lower blank activity levels, but using calcium phosphate results in much lower ^{226}Ra blanks.

The MDA for an actinide isotope using this method with alpha spectrometry was calculated according to equations prescribed by Currie: [11]

$$MDA = [3+4.65\sqrt{B}]/ (CT*R*V*Eff*0.060)$$

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

0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

The MDA for this method is flexible, as it depends on the sample aliquot and the count times used. In emergencies, short count times can be used while still being well below the estimated clinical decision guide target levels. Figure 6 shows MDA plotted for a 100 ml urine sample versus count time using ~25% efficiency alpha detectors and 90% chemical yield, with an assumption of 1 background count per 16 hours. The spot urine sample volumes collected following an emergency are often limited. In this case, a smaller urine aliquot can be used. For example, a 25 ml aliquot can be counted for 2 hours with an MDA of ~ 100 mBq L^{-1}, still less than estimated clinical decision guide target levels based on NCRP 161.

For small urine aliquots (25 ml or less), it is likely that 25mg Ca can be used to precipitate ^{226}Ra and that less cation resin could be used to remove Ca, with reduced column eluents and less preparation time. This will have to be tested. It may also be possible to adapt this method to allow measurement of ^{226}Ra by ICP-MS by adding a 2ml Sr Resin cartridge below the DGA cartridge to remove Sr and Ba, since ^{88}Sr + ^{138}Ba is a significant isobaric interference at m/z 226.

Conclusions

A new method has been developed that allows the rapid assay of ^{226}Ra in emergency urine samples by alpha spectrometry. The sample preparation method can be performed in <3 hours with chemical yields >90% and effective removal of interferences. The stacked elution technique using DGA Resin is a rapid effective approach that reduces sample preparation time. It is faster and offers some handling improvements over the use of Ln Resin.

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Figure 1 Rapid Sample Preparation Method for ^{226}Ra in Urine

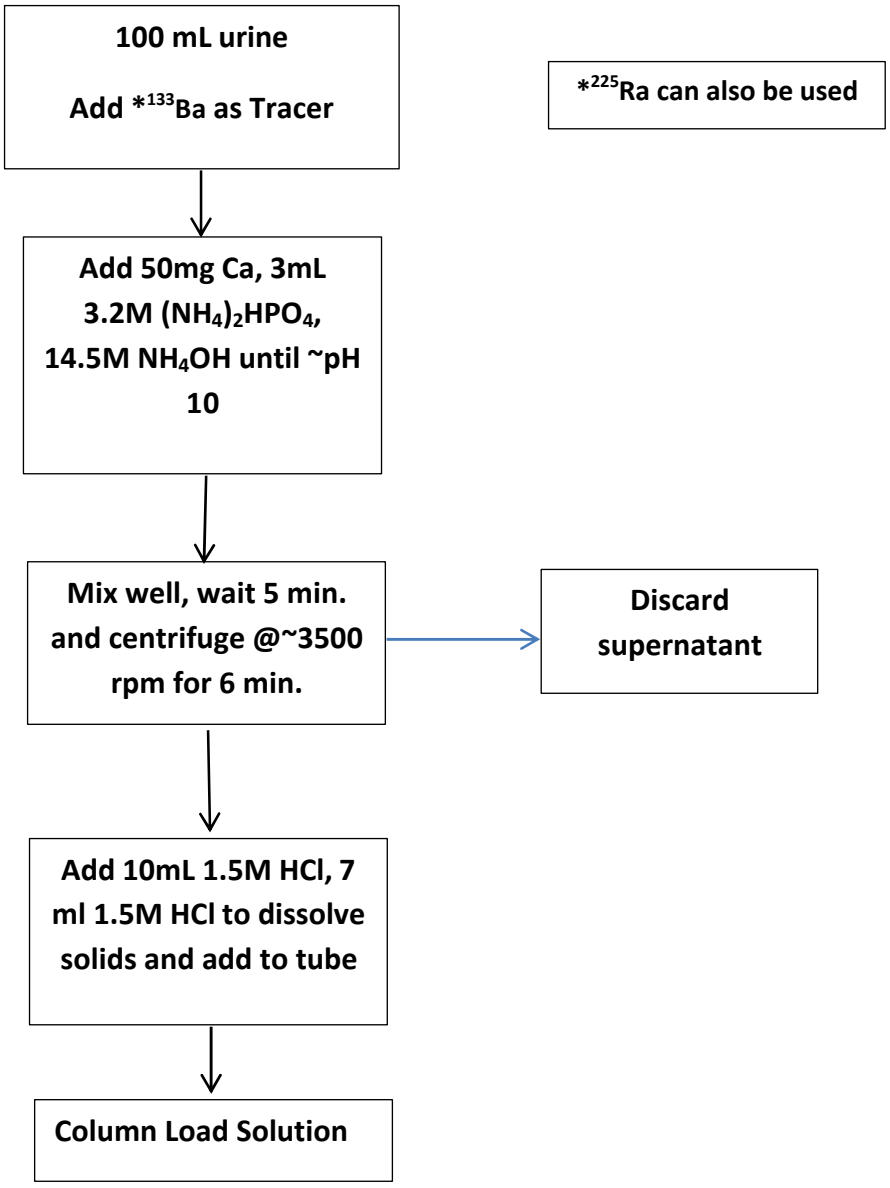

Figure 2 Rapid Column Separation Method for ^{226}Ra in Urine

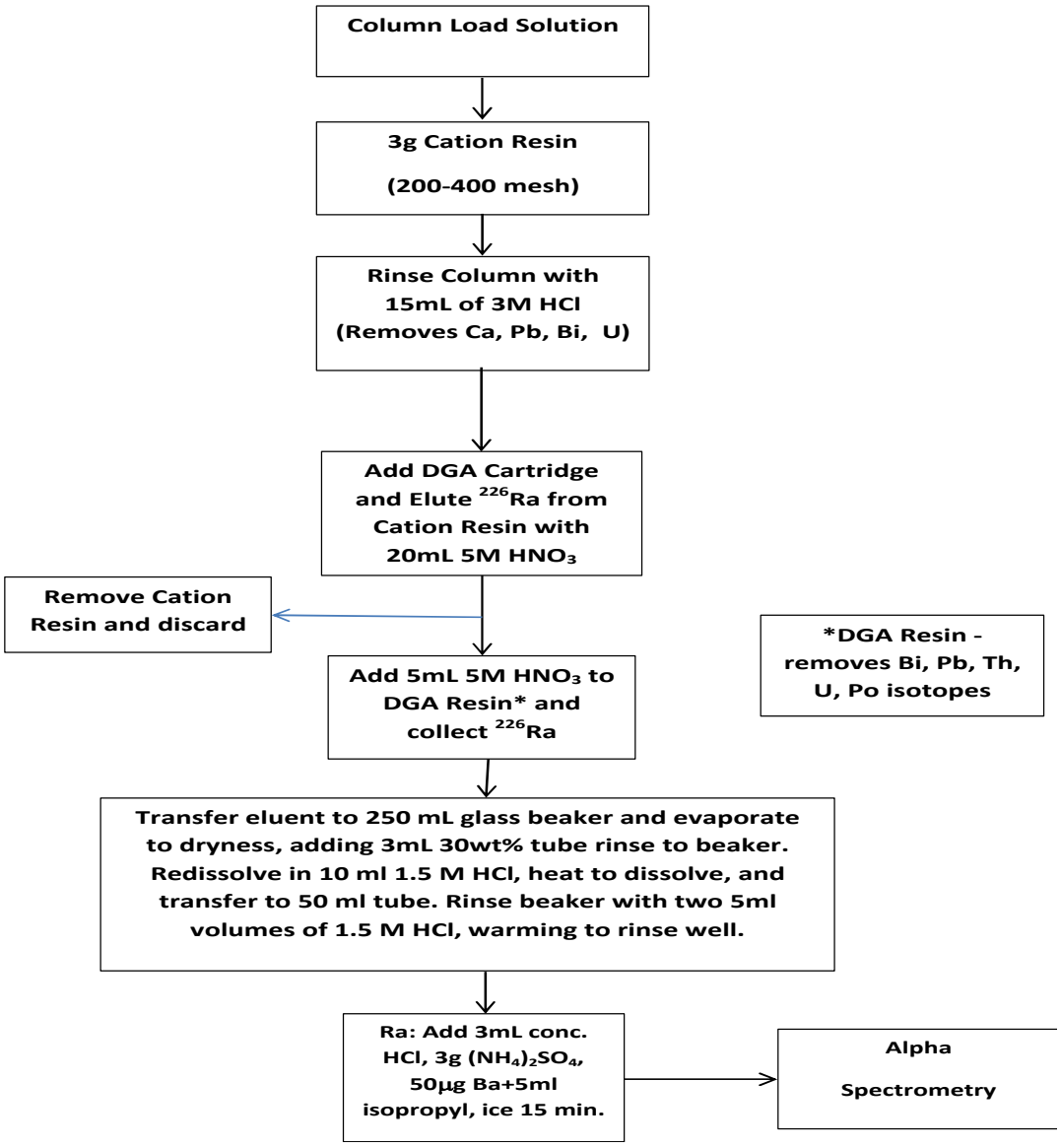

Figure 3 Calcium Removal during ^{226}Ra elution using DGA Resin

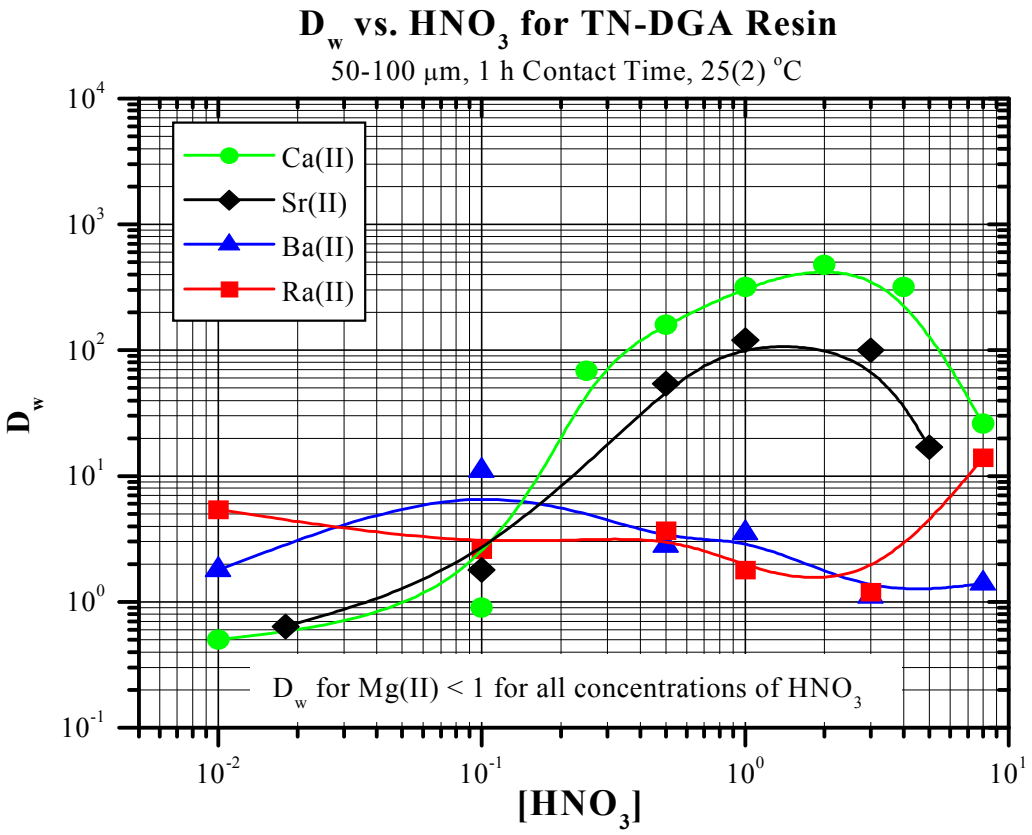

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Figure 4 Ra and Ba Elution Study on Cation Resin

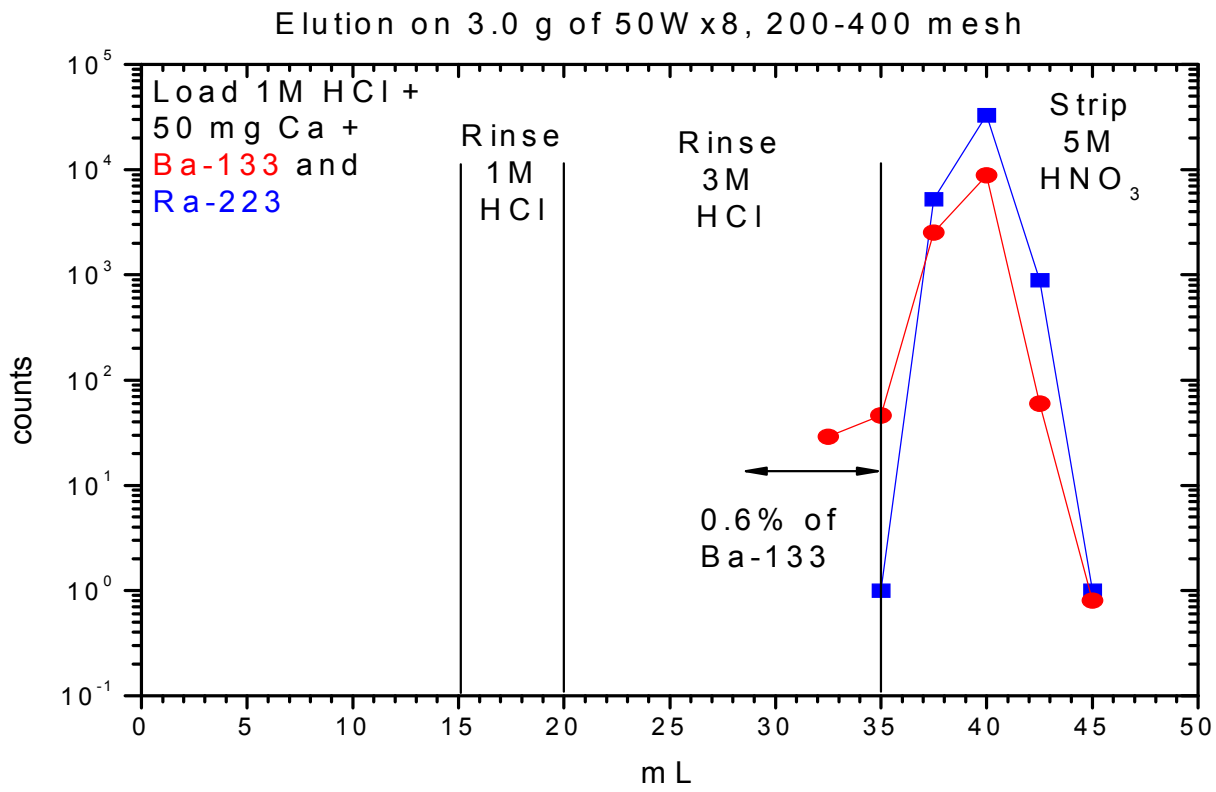

Figure 5 MDA for 100 ml Urine Aliquot vs. Count Time

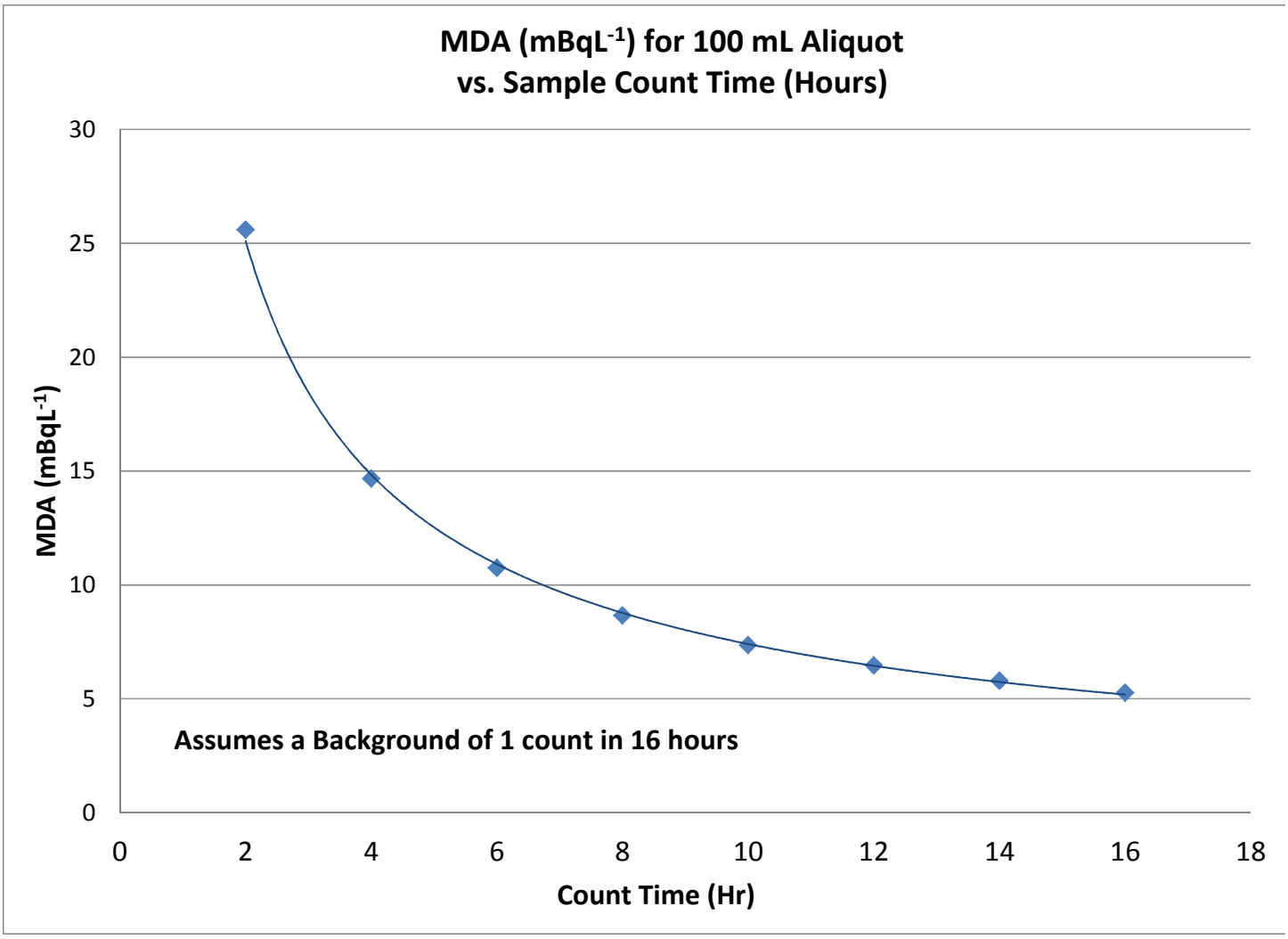

Table 1 ^{226}Ra Results on Spiked Urine - Cation + Ln Resin

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	97.3	73.67	73.4	-0.4
2	100.4	73.67	68.6	-6.9
3	96.8	73.67	71.8	-2.6
4	93.6	73.67	73.9	0.4
5	100.2	73.67	71.9	-2.4
6	90.0	73.67	70.4	-4.4
7	94.2	73.67	70.9	-3.8
8	98.2	73.67	71.1	-3.4
Avg	96.3		71.5	-2.9
SD	3.6		1.7	
% RSD	3.7		2.4	

For 100 ml aliquot 73.67 mBq/smp = 736.7 mBq/L

Table 2 ^{226}Ra Results on Spiked Urine - Cation + DGA Resin: Stacked Elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	95.4	73.67	82.9	12.6
2	96.6	73.67	70.6	-4.2
3	90.1	73.67	79.9	8.5
4	93.1	73.67	78.1	6.0
5	93.0	73.67	72.2	-2.0
6	88.8	73.67	75.3	2.2
Avg	92.8		76.5	3.9
SD	3.0		4.7	
% RSD	3.2		6.1	

For 100 ml aliquot 73.67 mBq/smp = 736.7 mBq/L

16 hour count

Table 3 ^{226}Ra Results on Spiked Urine - Cation + DGA Resin: Stacked Elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	100.4	18.42	18.4	-0.2
2	96.0	18.42	18.8	2.2
3	95.1	18.42	17.7	-3.9
4	101.2	18.42	17.9	-3.0
5	99.3	18.42	18.3	-0.8
6	96.1	18.42	16.5	-10.5
Avg	98.0		17.9	-2.7
SD	2.6		0.8	
% RSD	2.6		4.5	

For 100 ml aliquot 18.42 mBq/smp = 184.2 mBq/L

16 hour count

Table 4 ^{226}Ra Results on Blank Urine - Cation + DGA Resin: Stacked Elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Blank Result (pCi smp^{-1})	MDA (pCi smp^{-1})	^{226}Ra Blank Result (mBq smp^{-1})	MDA (mBq smp^{-1})
1	95.7	0.0016	0.017	0.058	0.629
2	94.7	0.0036	0.012	0.134	0.444
3	97.0	0.0026	0.014	0.096	0.518
4	84.0	0.0081	0.016	0.301	0.592
5	90.2	0.0077	0.015	0.285	0.555
6	92.7	0.0000	0.017	0.000	0.629
Avg	92.4	0.004	0.015	0.146	0.56
SD	4.7	0.003	0.002	0.122	0.07
% RSD	5.1				

100 ml sample aliquot

Blank test with 74 mBq ^{210}Po and ^{238}U added

0.146 mBq smp^{-1} = 1.46 mBq L^{-1}

16 hour count