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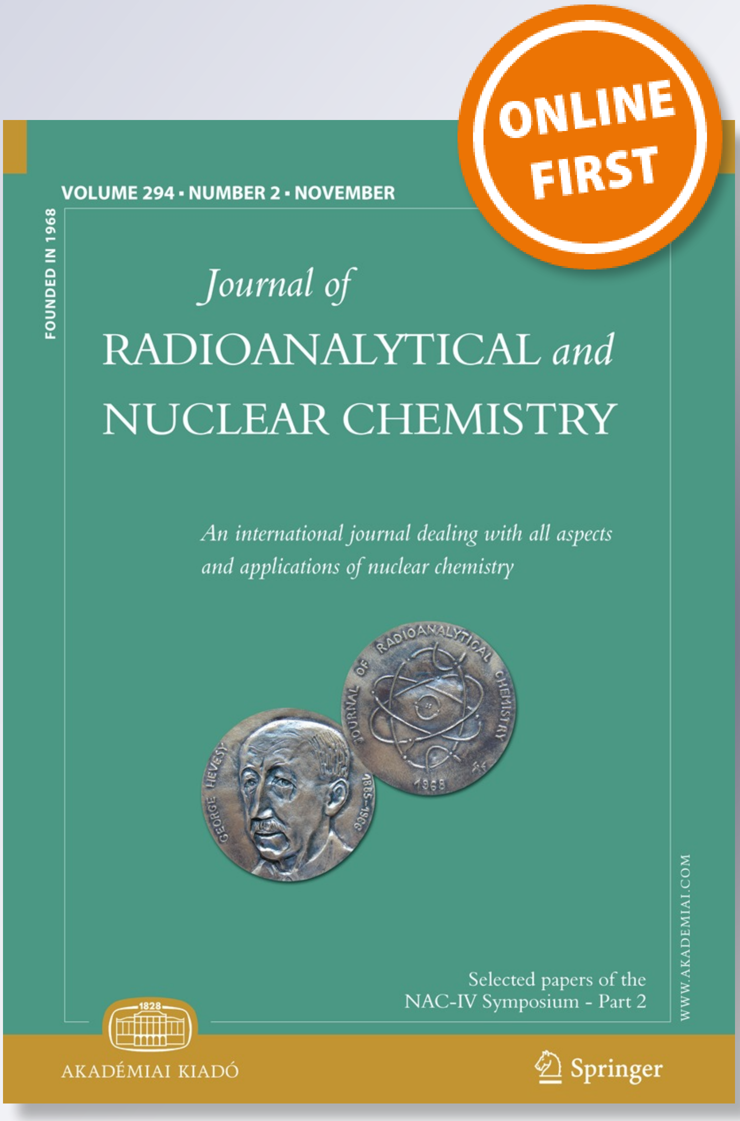

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Rapid method for determination of ^{228}Ra in water samples

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Abstract A new rapid method for the determination of ^{228}Ra in natural water samples has been developed at the SRNL/EBL (Savannah River National Lab/Environmental Bioassay Laboratory) that can be used for emergency response or routine samples. While gamma spectrometry can be employed with sufficient detection limits to determine ^{228}Ra in solid samples (via ^{228}Ac), radiochemical methods that employ gas flow proportional counting techniques typically provide lower minimal detectable activity levels for the determination of ^{228}Ra in water samples. Most radiochemical methods for ^{228}Ra collect and purify ^{228}Ra and allow for ^{228}Ac daughter ingrowth for $\sim$36 h. In this new SRNL/EBL approach, ^{228}Ac is collected and purified from the water sample without waiting to eliminate this delay. The sample preparation requires only about 4 h so that ^{228}Ra assay results on water samples can be achieved in <6 h. The method uses a rapid calcium carbonate precipitation enhanced with a small amount of phosphate added to enhance chemical yields (typically >90 %), followed by rapid cation exchange removal of calcium. Lead, bismuth, uranium, thorium and protactinium isotopes are also removed by the cation exchange separation. ^{228}Ac is eluted from the cation resin directly onto a DGA Resin cartridge attached to the bottom of the cation column to purify ^{228}Ac. DGA Resin also removes lead and bismuth isotopes, along with Sr isotopes and ^{90}Y. La is used to determine ^{228}Ac chemical yield via ICP-MS, but ^{133}Ba can also be used instead if ICP-MS assay is not available. Unlike some older methods, no lead or strontium holdback carriers or continual readjustment of sample pH is required.

Keywords Rapid · ^{228}Ra · ^{228}Ac · DGA Resin · Natural waters

Introduction

The measurement of radium isotopes in natural waters is important in the study of hydrospheric and geochemical processes, as well as for public health reasons. Large quantities of radium isotopes can be produced or accumulated as waste or by products from various industries, including phosphate mining and the oil and gas industry. Radium tends to accumulate in the bones of mammals due to chemical behavior similar to other alkaline earth metals (calcium, barium and strontium). As a result, the consumption of food and water containing radium isotopes by the general public, along with their short-lived radioactive progeny with high specific activities, can increase significantly the internal radiation dose of individuals [1]. Due to this potential toxicity of radium isotopes and their importance in geochemical studies related to mixing processes, the measurement of ^{226}Ra and ^{228}Ra in natural waters continues to be very important [2, 3]. Recently, new rapid methods for ^{226}Ra developed in the Savannah River National Lab/Environmental Bioassay Lab (SRNL/EBL, Aiken, SC, USA) were reported that provide rapid, effective assay of ^{226}Ra in a variety of environmental matrices [4]. ^{225}Ra (^{217}At), was used as a yield tracer in this rapid alpha spectrometry method, eliminating potential problems associated with ^{133}Ba tracer and Ra isotopes behaving differently.

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Many ^{228}Ra methods utilize liquid–liquid extraction using bis (2-ethylhexyl) phosphoric acid (HDEHP) to collect and purify ^{228}Ac to measure ^{228}Ra indirectly (after 36 h ingrowth). These solvent extraction techniques can be tedious and generate large amounts of liquid solvent waste. Burnett used Ln-Resin® (Eichrom Technologies, Lisle, IL, USA), which is a resin coated with HDEHP, to separate ^{228}Ac after a barium sulfate precipitation was used to collect radium from natural water samples. In this method, the barium sulfate precipitate had to be converted to barium carbonate in a heat bath for several hours. [5] Manganese dioxide (MnO_2)—coated fibers have been used for years for oceanographic analyses to collect radium for analysis. [3].

Nour et al. [6] also used MnO_2 precipitation and Diphonix Resin (Eichrom Technologies) to collect ^{228}Ra and ^{228}Ac. Stable strontium was added as a holdback carrier to try to minimize interference from Sr isotopes. ^{90}Sr, if not removed, will quickly regenerate ^{90}Y, which will follow ^{228}Ac on Diphonix Resin in this method. After ingrowth, ^{228}Ac was eluted with 1 M hydroxyethane-1,1 diphosphonic acid (HEDPA) and determined by liquid scintillation counting. The HEDPA was used because Ac(III) is very difficult to elute from Diphonix Resin. The use of HEDPA eluent typically precludes the use of gas flow proportional counting and subsequent separations, but it can be used by liquid scintillation or Cherenkov counting. Both techniques, however, typically have higher minimum detectable activity (MDA)'s than gas flow proportional counting. Aleissa et al. [7] also used the separation chemistry reported by Nour et al. but applied Cherenkov counting to determine ^{228}Ac instead of liquid scintillation. Sodium salicylate was added to increase ^{228}Ac efficiencies by Cherenkov counting from 10 to 38 %.

A combined ^{226}Ra/^{228}Ra method was reported by the SRNL/EBL lab that utilized MnO_2 Resin (Eichrom Technologies) to collect radium from water samples. The ^{228}Ra method required a 30 h ingrowth period for the ingrowth of ^{228}Ac, prior to separation using DGA Resin. The method used ^{133}Ba as a yield monitor for both the ^{226}Ra and ^{228}Ra measurements [8]. While there were some advantages to using MnO_2 Resin, the previous work did not have a ^{228}Ac yield monitor that was also retained and eluted from the DGA Resin. The method also required an ingrowth period for ^{228}Ac.

Based on a survey of the scientific literature, there still seemed to be a need for an improved rapid ^{228}Ra method, especially if the there is a desire to collect the ^{228}Ac from water samples without waiting for ingrowth. Since MnO_2 Resin or MnO_2 precipitation may not collect ^{228}Ac quantitatively under certain sample matrix conditions, another separation approach was investigated.

A new rapid method for the determination of ^{228}Ra in natural water samples has been developed at the SRNL/EBL Laboratory that can be used for emergency response or routine samples. While gamma spectrometry can usually be employed with sufficient detection limits to determine ^{228}Ra in solid samples (via ^{228}Ac), radiochemical methods that employ gas flow proportional counting techniques typically provide lower MDA levels for ^{228}Ra assay for a water sample matrix. Most radiochemical methods for ^{228}Ra collect and purify ^{228}Ra and allow for ^{228}Ac daughter ingrowth for $\sim$36 h. In this new SRNL/EBL approach, ^{228}Ac is collected and purified from the water sample without waiting to eliminate this delay. The sample preparation requires only about 4 h so that ^{228}Ra assay results on water samples can be achieved in <6 h. This new approach for the assay of ^{228}Ra offers an improved yield measurement for ^{228}Ac and a rapid option to collect ^{228}Ac without waiting for ingrowth.

The method uses a rapid calcium carbonate precipitation enhanced with a small amount of phosphate to enhance chemical yields (typically >90 %), followed by rapid cation exchange removal of calcium. Lead, bismuth, uranium, thorium and protactinium isotopes are also removed by the cation exchange separation [9]. ^{228}Ac is eluted from cation resin directly onto a DGA Resin cartridge attached to the cation column. DGA Resin is used to purify ^{228}Ac, also removing lead and bismuth isotopes, along with Sr isotopes and ^{90}Y. La is used to determine ^{228}Ac chemical yield via inductively-coupled plasma-mass spectrometry (ICP-MS), but ^{133}Ba can also be used instead if ICP-MS assay is not available.

Unlike other methods, the method outlined in this work does not require any liquid solvents such as HDEHP, does not need a carbonate conversion of barium sulfate for hours in a heat bath, does not require precise load solution acidity adjustments with Ln Resin, and does not require waiting 36 h for ^{228}Ac ingrowth. However, ^{228}Ac ingrowth is an option if desired. Unlike some older methods, no holdback carriers or continual readjustment of sample pH is required.

If ^{139,141}Ce, ^{147}Nd and ^{140}La radionuclides are present due to a mixed fission product release, one can collect the purified ^{228}Ra from the sample after rapid removal of these lanthanides using DGA Resin and reprocess the samples through DGA Resin again after ingrowth of ^{228}Ac.

The method ruggedness, as indicated by high chemical yields and effective removal of interferences, including high levels of ^{90}Sr, makes this method useful for environmental laboratories.

Experimental

Reagents

The resins employed in this work are Cation Resin (50 W-X8, Hydrogen form, 200–400 mesh) and DGA

Resin (*N,N,N′,N′* tetraoctyldiglycolamide, available from Eichrom Technologies, LLC (Lisle, IL, USA). Nitric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2^{TM} water purification system. All other materials were ACS reagent grade. The radiochemical isotope ^{228}Ra was obtained from Eckert and Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq m/L. ^{90}Sr, ^{226}Ra, and ^{238} U standards were also obtained from Eckert and Ziegler/Analytics, Inc.

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 and adding to in large ion exchange column reservoirs (Environmental Express, Mount Pleasant, SC, USA). DGA Resin cartridges containing 2 mL of each resin were obtained from Eichrom Technologies, (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 were typically used.

The separation utilizes removal of interferences using both cation exchange resin and DGA Resin. The cation resin effectively removes large amounts of calcium used to precipitate the ^{228}Ra, ^{228}Ac and La ions from water samples, as well as other interferences. While calcium, strontium and lead ions are all strongly retained on DGA Resin in 3 M HNO_3, they are all effectively removed using much stronger nitric acid. Since there is much less retention of Ca, Sr and Pb ions in 7 M HNO_3, this acid concentration was selected to elute La, Ac and Ra from the cation resin through DGA Resin [10]. Figure 1 shows how Ac^{3+} retention on DGA Resin is still significant ($k' > 100$) in 7 M HNO_3. This nitric acid concentration was selected to remove Ca, Sr and Pb ions, while retaining Ac and La ions on DGA Resin. The k′ values were measured using the batch extraction procedure and calculations described in reference [11].

Figure 1 also shows how Ac^{3+} can be eluted from DGA Resin using 2 M HCl. Under these conditions, Y, Po and Bi ions (as well as heavier lanthanide isotopes such as Eu, Gd) will be retained. Figure 2 shows the k′ retention values are very low for La in 2 M HCl, while Y is retained.

Sample preparation

Replicate sample aliquots of various water samples were added to 1 liter glass beakers. Tap water and well water samples were spiked with varying levels of ^{228}Ra.

Figure 3 shows the rapid precipitation steps that can be used for aqueous environmental samples to preconcentrate the ^{228}Ra from a water matrix. Water sample aliquots of 1 liter were acidified to ~pH 2 in glass beakers using nitric acid. To each test batch of replicate water samples, varying levels of ^{228}Ra were added to each replicate sample. Water sample batches were spiked with ^{228}Ra at 177.2 mBq/L (4.78 pCi/L), 354.5 mBq/L (9.57 pCi/L), and 1,046 mBq/L (28.2 pCi/L) respectively. A blank replicate was also analyzed with each batch so that the ^{228}Ra results could be corrected for the native content of ^{228}Ra. Lanthanum (La) tracer (1 mg) was added to each sample. Barium carrier (5 mg) was added to each sample to enhance precipitation efficiency. Three milliliters of 1.25 M calcium nitrate (150 mg Ca) and 1 mL of 3.2 M ammonium hydrogen phosphate were added to each water sample. Thirty milliliters of concentrated ammonium hydroxide (14.5 M) were added to each sample beaker and each solution was mixed. Thirty milliliters of 2 M sodium carbonate were added to each sample beaker. Each sample was stirred and placed on a hot plate on high heat for about 30 min or until very hot to reduce the impact of any dissolved CO_2 in the samples and to reduce solubility.

The beakers were removed from the hot plate and the precipitate was allowed to settle. The supernatant was poured off down to about 200 mL volume so that the remaining sample and solids could be transferred to 225 mL centrifuge tubes. The tubes were centrifuged at 3,500 rpm for 5 min and the supernatant was discarded. The remaining solids were dissolved in 10 mL of 1.5 M HCl, and transferred to a 50 mL centrifuge tube. The 225 mL tube was rinsed well with 7 mL of 1.0 M HCl and this rinse solution was added to each dissolved sample. If any residual solids remained, they were rinsed well by mixing with 5 mL 1.5 M HCl, and centrifuging to remove any residual solids. This rinse was added to the original sample solution.

Samples were loaded to columns containing 5.0 g of Cation Resin (200–400 mesh). The bed height of the columns was about 4 cm and each column was conditioned with ~25 mL of deionized water and 10 mL of 0.5 M HCl. Gravity flow was typically sufficient to achieve a flow rate of ~1 drop/s, however vacuum was applied if needed.

Column separation

Figure 4 shows the rapid column separation sequence used. The Ra, Ac and La were retained on cation resin (5 g) and calcium was removed by rinsing with 2.75 M HCl-0.02 M HF at ~1 drop/s. HF was used in this HCl rinse step to help stabilize any Pa^{5+} ions that might be present, so they would pass through the cation resin without adhering to the plastic surfaces such as the polyethylene frits in the cation

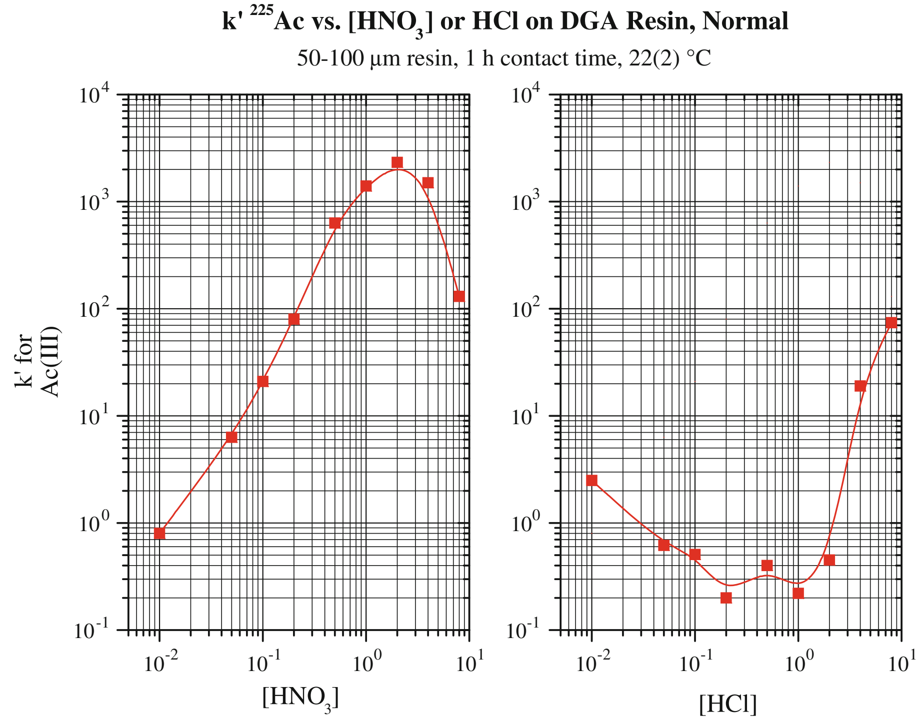

Fig. 1 Retention of Ac(III) on DGA resin courtesy PG Research Foundation, Lisle, IL, USA

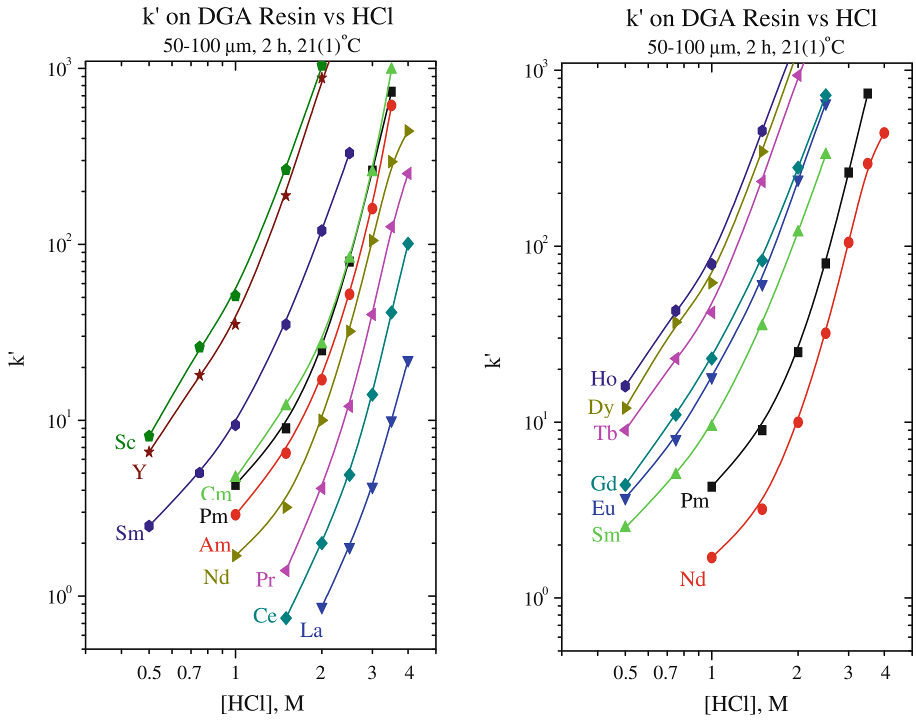

Fig. 2 Retention of lanthanides and yttrium on DGA resin in HCl courtesy PG Research Foundation, Lisle, IL, USA

column. A 2 mL DGA Resin cartridge was placed below each cation resin column and ^{228}Ac and La were eluted from the cation resin with 25 mL 7 M HNO_3 onto DGA Resin at ~1 drop/s, while Ra passed through. The separation time was taken as the mid-point of this elution step to accurately determine and correct for any decay of ^{228}Ac in the following separation and counting steps. The cation resin column was removed and DGA Resin alone was rinsed with 5 mL 7 M HNO_3 to further enhance the removal of Sr and Pb isotopes.

^{228}Ac and La were eluted with 19 mL 2 M HCl at ~1 drop/s. The eluent volumes were adjusted to exactly 20 mL volume with 2 M HCl and mixed well. One hundred microliters of each sample were transferred to 50 mL

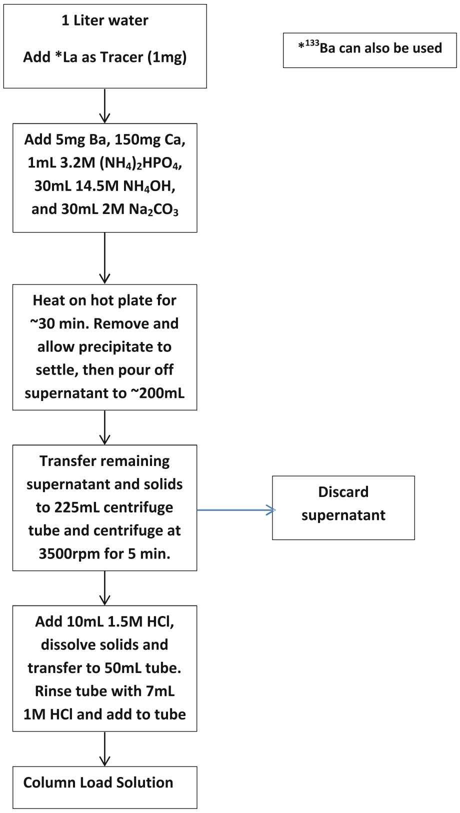

Fig. 3 Rapid ^{228}Ra sample preparation for water samples

centrifuge tubes for dilution to 50 mL and ICP-MS measurement of La (~100 ng/mL).

Microprecipitation

To each final purified solution containing 20 mL 2 M HCl, 100 µg cerium and 3 mL 28 M HF were added. While the rare earth La was already present in the purified solution, Ce was included in the method in case La tracer was inadvertently omitted or to allow for the use of ^{133}Ba tracer instead. After mixing well, the tubes were allowed to sit for ~15 min. The solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve ®-Filter-Eichrom Technologies), rinsing the filters with 95 % ethanol. The filters were dried under a heat lamp and counted by gas flow proportional counting.

Apparatus

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 mL plastic tubes were used to perform the column separations.

The ^{228}Ac samples are counted simultaneously using a thin (Mylar) windowed Tennelec LB 4100 Gas Flow Proportional Counter system. A high detection efficiency (>50 %) and low detector background (<2 cpm) results in detection levels typically <1 pCi/L for 60 min count times. Results are decay corrected from the midpoint of the count time back to the midpoint of the elution time.

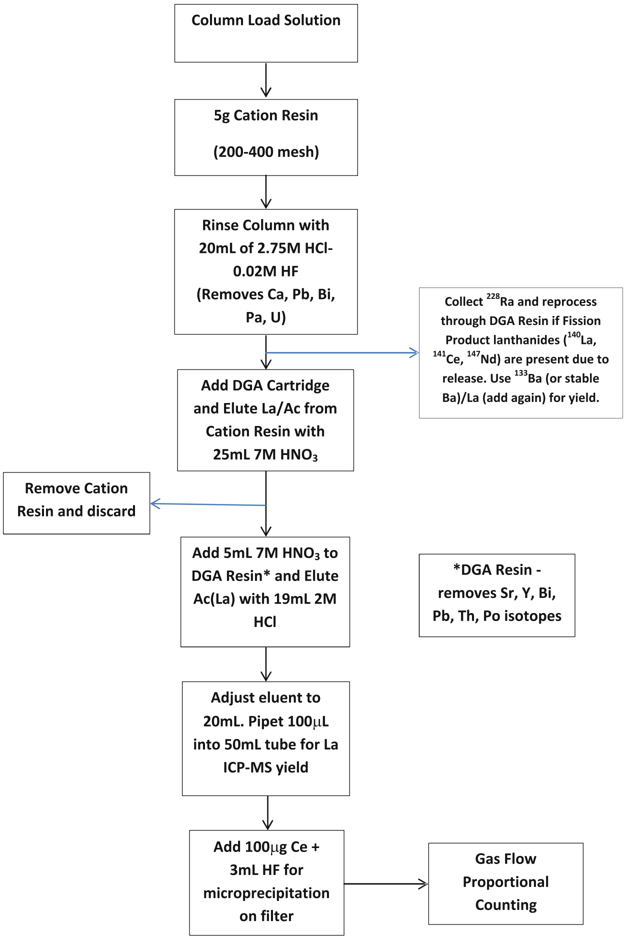

Fig. 4 Rapid ^{228}Ra column separation for water samples

A Perkin Elmer Elan DRC-e (using standard ICP-MS mode) was used to perform the ICP-MS measurements. Instrument operating conditions are shown in Table 1.

Results and discussion

Table 2 shows the individual results for the determination of ^{228}Ra (spiked at 177.2 mBq/L) in seven one liter tap water samples using this rapid separation method and gas flow proportional counting. The ^{228}Ac/^{228}Ra results were corrected for La tracer yield using ICP-MS. The average ^{228}Ra result for the one liter tap water samples was 177.5 mBq/L, with a 0.2 % bias and 1 SD (standard deviation) of 20.5 mBq/L. The measured values were corrected for 21.5 mBq ^{228}Ra found in the unspiked water sample. The high La (^{228}Ac) tracer recoveries and excellent results for the analytes versus known values indicate the ruggedness of the sample preparation and measurement

Table 1 Operating conditions for Perkin Elmer Elan DRC-e

Plasma conditions	
RF Power	1,400 W
Torch depth	5.5 mm
Plasma gas	15 L/min
Carrier gas	1 L/min
Nebulizer gas	0.98 L/min
Sample pump	5 rps
Ion lens/quadrupole	
E1 lens voltage	6.25 V
E1 lens slope	0.0165
E1 lens intercept	4.413
Cell path voltage	−12 CPV
Cell Rod offset	−17 V
Q-pole rod offset	−4 V
Detector	
Discriminator	17 V
Analog HV	−1,550 V
Pulse HV	900 V
Typical tune	
Counts	>300,000 cps In-115 at 10 μg/L
RSD %	<5 %
Oxide 156/140	<5 %
Background	<10 cps at mass 220; < 10 cps at mass 8.5 (vacant mass -noise detection only)
Resolution	0.60–0.80 amu at 10 % peak height
Data acquisition	
Integration	1,000 ms dwell time 50 ms
Replicates	3 with 20 sweeps/reading

steps for the water samples. The average tracer recovery for La was 94.1 % ± 2.3 % at 1 SD.

Table 3 shows the individual results for the determination of ^{228}Ra (spiked at 354.5 mBq/L) in seven one liter tap water samples using this rapid separation method and gas flow proportional counting. The ^{228}Ac/^{228}Ra results were corrected for La tracer yield using ICP-MS. The average ^{228}Ra result for the one liter tap water samples was 347.2 mBq/L, with a −2.1 % bias and 1 SD (standard deviation) of 24.8 mBq/L. The measured values were corrected for 21.5 mBq ^{228}Ra found in the unspiked water sample. The La (^{228}Ac) tracer recoveries were very good and very consistent. The average tracer recovery for La was 91.8 % ± 1.2 % at 1SD.

Table 4 shows the individual results for the determination of ^{228}Ra (spiked at 1,046 mBq/L) in six one liter groundwater samples using this rapid separation method and gas flow proportional counting. The ^{228}Ac/^{228} Ra results were corrected for La tracer yield using ICP-MS. The average ^{228}Ra result for the 1 L tap water samples was 1,008.3 mBq/L, with a −3.6 % bias and 1 SD (standard deviation) of 27.8 mBq/L. The measured values were corrected for 174.2 mBq ^{228}Ra found in the unspiked water sample. The average tracer recovery for La (^{228}Ac) was 95.3 % ± 0.9 % at 1 SD.

Table 5 shows the individual results for the determination of ^{228}Ra in one liter water samples with varying levels of interferences added. ^{90}Sr/^{90}Y at 5.92 Bq and 29.6 Bq levels respectively were added to separate sets of 4 water samples spiked with 1.046 Bq ^{228}Ra. In addition, 3.7 Bq ^{238}U and 4.81 Bq ^{226}Ra were added to 4 sets of water samples also spiked with 1.046 Bq ^{228}Ra. The overall ^{228}Ra recoveries are ~95 % for each set of samples spiked with interferences, with no significant positive bias in the ^{228}Ra results for these ratios of ^{90}Sr/^{90}Y, ^{238}U and ^{226}Ra added. It was particularly encouraging to see no apparent Sr/Y carryover into the ^{228}Ac fraction despite the addition of 800 pCi (29.6 Bq), considering the difficulties that some ^{228}Ra methods have with interference from Sr/Y. The removal of ^{226}Ra progeny such as ^{214}Pb and ^{214}Bi daughters was also confirmed, despite adding ^{226}Ra/^{228}Ra ratios of almost 5–1. A more precise decontamination study can be performed using water blanks, but considering the typical Ra, U and Sr levels and ratios in natural waters this test was still very useful, indicating excellent removal of typical interferences.

Table 6 shows the results from spiked water blanks with 1,000 pCi/L (37,000 mBq/L) of ^{90}Sr/^{90}Y added, counted with a 10 h count time. The average blank activity of 0.244 pCi/L (9.01 mBq/L) was very close to the average MDA of 0.202 pCi/L (7.46 mBq/L). While the blank results may have a slight positive bias relative to zero, this bias in the blank values is not considered to be significant from a practical standpoint. A decontamination factor was calculated for each blank measurement by dividing the initial 1,000 pCi (37,000 mBq) of ^{90}Sr/^{90}Y added by the final blank measurement. The average decontamination factor for ^{90}Sr/^{90}Y was 4,230 (1SD = 797), indicating an average ^{90}Sr/^{90}Y removal of 99.97 %.

The MDA for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie: [11].

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

where B = total background counts, = BKG (rate) * BKG count time, CT = sample count time (min), R = chemical recovery, W = sample aliquot (L), Eff = detector efficiency, 0.060 = conversion from dpm to mBq

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

The MDA for the ^{228}Ra results can be adjusted as needed, depending on the sample aliquot and count time. This method provides a typical MDA of ~18.5 mBq/L (0.5 pCi/L) for a 90 min count time for a 1 L sample water sample. Longer count times can be used to lower MDA levels as needed.

Table 2 ^{228}Ra results for water samples (177 mBq/L level)

Sample ID	La (Ac) Yield (%)	^{228}Ra reference value (pCi/L)	^{228}Ra reference value (mBq/L)	^{228}Ra measured value (mBq/L)	Difference (%)
1	93.4	4.79	177.2	160.5	−9.47
2	92.1	4.79	177.2	169.2	−4.51
3	95.3	4.79	177.2	167.4	−5.54
4	97.8	4.79	177.2	193.1	8.98
5	91.6	4.79	177.2	215.7	21.72
6	94.4	4.79	177.2	158.4	−10.61
7	95.6	4.79	177.2	178.3	0.60
Avg	94.3			177.5	0.2
SD	2.2			20.5	
% RSD	2.3			11.6	

90 min count time

1 L sample aliquot

La (Ac) yield by ICP-MS

Measured values corrected for 21.5 mBq per liter native ^{228}Ra content

Table 3 ^{228}Ra results for water samples (354.5 mBq/L level)

Sample ID	La (Ac) yield (%)	^{228}Ra Reference value (pCi/L)	^{228}Ra Reference value^{228} (mBq/L)	Ra Measured value (mBq/L)	Difference (%)
1	92.0	9.58	354.5	331.7	−6.4
2	93.1	9.58	354.5	380.9	7.5
3	93.1	9.58	354.5	309.2	−12.8
4	91.1	9.58	354.5	356.1	0.5
5	91.6	9.58	354.5	329.4	−7.1
6	90.1	9.58	354.5	367.0	3.6
7	94.0	9.58	354.5	355.9	0.4
Avg	92.1			347.2	−2.1
SD	1.3			24.8	
% RSD	1.5			7.1	

60 min count time

1 L sample aliquot

La (Ac) yield by ICP-MS

Measured values corrected for 21.5 mBq per liter native ^{228}Ra content

New resin cartridges were used for each analysis to minimize any chance of cross-contamination of samples or unexpected degradation of performance, which can occur over time and may be different than the anticipated reuse rate depending on real world sample matrix variation. Some laboratories, however, have had success reusing resins. It is anticipated that DGA Resin can potentially be reused after rinsing the resin cartridges with 0.25 M HCl.

Table 4 ^{228}Ra results for ground water samples (1,046 mBq/L level)

Sample ID	La (Ac) Yield (%)	^{228}Ra reference value (pCi/L)	^{228}Ra reference value (mBq/L)	^{228}Ra measured value (mBq/L)	Difference (%)
1	94.9	28.28	1,046.4	1,033.6	−1.2
2	95.7	28.28	1,046.4	1,045.4	−0.1
3	96.2	28.28	1,046.4	1,017.1	−2.8
4	94.5	28.28	1,046.4	992.0	−5.2
5	96.4	28.28	1,046.4	982.5	−6.1
6	94.3	28.28	1,046.4	979.3	−6.4
Avg	95.3			1,008.3	−3.6
SD	0.9			27.8	
% RSD	0.9			2.8	

60 min count time

1 liter sample aliquot

La (Ac) yield by ICP-MS

Measured values corrected for 174.2 mBq per liter native 228Ra content

The use of stable La as a tracer for ^{228}Ac provided a very effective yield measurement. The rare earth fluoride sample source mount was effective, and does not require any consideration of hydroscopic impacts on a carrier precipitate, such as yttrium oxalate, for yield As an alternative to La by ICP-MS, ^{133}Ba can be added and used to determine yield. The 7 M HNO_3 load solution can be collected after it passes through DGA Resin and counted by gamma spectrometry.

If sediment is present in the water samples, the sediment can be filtered on a glass fiber filter, for example, and a rapid sodium hydroxide fusion can be applied [4]. The fusion matrix can be dissolved in water and added back to the 1 liter water sample if a combined water/sediment ^{228}Ra result is desired. If separate assays are preferred, the same preconcentration chemistry can be applied. The calcium carbonate/phosphate precipitation steps can be used after transferring the alkaline fusion matrix to a 225 mL centrifuge tube collect the ^{228}Ra/^{228}Ac in the sediment, allowing for the hydroxide added from the fusion material.

The method assumes ^{228}Ra/^{228}Ac equilibrium, a reasonable assumption especially 36 h after the water sample is preserved by adjusting the acidity to pH 2. Water samples are often preserved at the field collection point, however, if not, the samples may be held 36 h after adjusting to pH 2 in the lab, or alternately the sample precipitate may be held 36 h to allow ingrowth of ^{228}Ac as well. It is likely, however, that water samples, unless they contain significant amount of sediment, are in equilibrium prior to sample pH adjustment.

While it would seem the rapid ^{226}Ra [4] and rapid ^{228}Ra methods recently developed by the SRNL/EBL lab could

Table 5 ^{228}Ra results with interferences added

Interference added	^{90}Sr/^{90}Y	^{90}Sr/^{90}Y	^{238}U	^{226}Ra
	5.92 Bq	29.6 Bq	3.7 Bq	4.81 Bq
1.046 Bq ^{228} Ra added	^{228}Ra recovery (%)	^{228}Ra recovery (%)	^{228}Ra recovery (%)	^{228}Ra recovery (%)
1	95.7	92.7	99.4	92.7
2	94.9	96.0	93.0	103.0
3	98.8	89.8	94.5	95.9
4	96.5	93.4	94.4	88.1
Avg. ^{228}Ra Recovery (%)	96.5	93.0	95.3	94.9
SD	1.7	2.6	2.8	6.3

Table 6 Blank results with 1,000 pCi/L (37 Bq/L) ^{90}Sr added

	MDC (pCi/L)	Blank sample (pCi/L)	MDC (mBq/L)	Blank sample (mBq/L)	Decontamination factor (Sr/Y)
1	0.20	0.19	7.35	7.02	5,267
2	0.21	0.25	7.85	9.13	4,054
3	0.19	0.25	7.18	9.35	3,956
4	0.21	0.32	7.64	11.68	3,166
5	0.20	0.21	7.26	7.86	4,707
Avg.	0.202	0.244	7.456	9.010	4,230
SD	0.008	0.048	0.280	1.771	797
% RSD	3.8	19.7	3.8	19.7	18.8

10 h count time

be combined into a single method, this would likely preclude the use of ^{225}Ra as a tracer, due to beta-emitting progeny in the ^{225}Ra decay chain. For labs that elected to use ^{133}Ba instead, combining these two approaches could very well be a viable option, with associated cost benefits.

Conclusions

A new rapid method to determine ^{228}Ra in natural water samples has been developed that allows the separation of ^{228}Ra with high chemical yields and effective removal of interferences. The new method uses a rapid calcium carbonate precipitation enhanced with a small amount of phosphate to enhance chemical yields (typically >90 %), followed by rapid cation exchange removal of calcium and other interferences. Lead, bismuth, uranium, thorium and protactinium isotopes are also removed by the cation exchange separation. ^{228}Ac is eluted from cation resin directly onto a DGA Resin cartridge attached to the cation resin column.to purify ^{228}Ac. DGA Resin also removes lead and bismuth isotopes, along with Sr isotopes and ^{90}Y. La is used to determine ^{228}Ac chemical yield via inductively-coupled plasma-mass spectrometry (ICP-MS), but ^{133}Ba can also be used instead if ICP-MS assay is not available.

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