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Rapid Method for Ra-226 and Ra-228 in Water Samples

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Abstract

The measurement of radium isotopes in natural waters is important for oceanographic studies and for public health reasons. Ra-226 (1620 year half-life) is one of the most toxic of the long-lived alpha emitters present in the environment due to its long life and its tendency to concentrate in bones, which increases the internal radiation dose of individuals. The analysis of radium-226 and radium-228 in natural waters can be tedious and time-consuming. Different sample preparation methods are often required to prepare Ra-226 and Ra-228 for separate analyses. A rapid method has been developed at the Savannah River Environmental Laboratory that effectively separates both Ra-226 and Ra-228 (via Ac-228) for assay. This method uses MnO_2 Resin from Eichrom Technologies (Darien, IL, USA) to preconcentrate Ra-226 and Ra-228 rapidly from water samples, along with Ba-133 tracer. DGA Resin® (Eichrom) and Ln-Resin® (Eichrom) are employed in tandem to prepare Ra-226 for assay by alpha spectrometry and to determine Ra-228 via the measurement of Ac-228 by gas proportional counting. After preconcentration, the manganese dioxide is dissolved from the resin and passed through stacked Ln-Resin-DGA Resin cartridges that remove uranium and thorium interferences and retain Ac-228 on DGA Resin. The eluate that passed through this column is evaporated, redissolved in a lower acidity and passed through Ln-Resin again to further remove interferences before performing a barium sulfate microprecipitation. The Ac-228 is stripped from the resin, collected using cerium fluoride microprecipitation and counted by gas proportional counting. By using vacuum box cartridge technology with rapid flow rates, sample preparation time is minimized.

Key Words

Water

Ra-226

Ra-228

Extraction chromatography

Separations

Manganese dioxide Resin

Introduction

The measurement of radium isotopes in natural waters is important for oceanographic studies (1) and for public health reasons (2). Ra-226 (1620 year half-life) is one of the most toxic of the long-lived alpha emitters present in the environment due to its long life and its tendency to concentrate in bones, which increases the internal radiation dose of individuals. The measurement of radium-226 and radium-228 in natural waters can be tedious and time-consuming. Different sample preparation methods are often required to prepare Ra-226 and Ra-228 for analysis. Few simple and selective methods are available for the preparation for radium isotopes and of concern is the use of a suitable tracer that matches the chemical behavior of radium. (3) Ra-226 is measured either by radon emanation of alpha spectrometry. Radon emanation, however, is a slow, indirect measurement that has sample handling difficulties due to the gaseous nature of radon-222. Barium sulfate co-precipitation can be used to concentrate samples for alpha spectrometry but it can be tedious and analyst-dependent. Most Ra-228 methods utilize liquid-liquid extraction using bis (2-ethylhexyl) phosphoric acid (HDEHP) to collect and purify Ac-228 to measure Ra-228 indirectly. Burnett used Ln-Resin ®, which is a resin coated with HDEHP, to separate Ac-228 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 (4). A similar approach has been used by Thakkar to separate Ra-228 (via Ac-228) after preconcentration on cation resin (5). The Ra-228 was stripped from the cation resin using 8M HNO3. This solution was evaporated and the acidity had to be adjusted very carefully to 0.09M HNO3. If the acidity is not precisely controlled, Ac-228 losses on Ln-Resin can occur. The cation method also has some sensitivity to calcium and magnesium interference, and was limited to 100 mL samples size when a total calcium and magnesium level >200 ppm was present. Large cation columns may also have the disadvantage of slow column flow for water samples with particulates. Manganese dioxide (MnO_2) –coated fibers have been used for years for oceanographic analyses to collect radium for analysis (6). Bojanowski used hydrous MnO_2 to collect Ra-226 from natural waters but this approach requires two separate precipitations to achieve quantitative results. (7) Burnett has used MnO_2 Resin from Eichrom Technologies (Darien, IL, USA) to separate radium from natural waters for analysis using an automated analyzer. He has reported good retention of barium and radium between pH 4 and pH 8. (8) Sato has used Mn impregnated fibers to collect Radium-226 and Ra-228 from very large water samples. Burnett has also used manganese-impregnated fibers to collect Ra-226 and Ra-228 from 20 to 150 liters of seawater and groundwater samples for gamma spectrometry determination. (9)

A rapid method has been developed at the Savannah River Environmental Laboratory using MnO_2 Resin (Eichrom Technologies, Darien, IL, USA) that effectively separates and prepares both Ra-226 and Ra-228 (via Ac-228) for assay by alpha spectrometry and gas proportional counting, respectively. Ba-133 tracer is used in this method to successfully measure chemical yield. This method uses MnO_2 Resin to rapidly preconcentrate Ra-226 and Ra-228 from water samples, along with the Ba-133 tracer. DGA Resin® (Diglycolamide Resin, Eichrom) and Ln-Resin® (Eichrom) are employed in tandem to prepare Ra-226 for assay by alpha spectrometry and to determine Ra-228 via the measurement of Ac-228 by gas proportional counting. Vacuum box technology with an inner liner to collect large volumes of sample passed through the MnO_2 resin is used to make the separation more rapid. This approach also allows the operator to apply increased vacuum to any “stubborn” columns that do not flow as fast as others in the batch . The new SRS water method is a rapid, easy to use method that effectively separates and prepares both Ra-226 and Ra-228 (via Ac-228) for analysis.

Experimental

Reagents

The resins employed in this work are MnO_2 Resin, DGA Resin (N,N,N’,N’ tetraoctyldiglycolamide), Ln-Resin (bis (2-ethylhexyl) phosphoric acid) available from Eichrom Technologies, Inc., (Darien, Illinois, USA). Hydrochloric acid 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 and were used as received. Radiochemical isotope standards Ba-133, Ra-226, and Ra-228 were obtained from Analytics, Inc. (Atlanta, GA, USA). Ba-133 was diluted to ~1000 pCi/mL and Ra-226 and Ra-228 standards were diluted to ~10 pCi/mL.

A barium sulfate seeding suspension was prepared by placing 11.3 mg of barium chloride, dihydrate ($BaCl_2.2H_20$), 10 mL of the 70% sodium sulfate solution in a 250 mL Erlenmeyer flask. This solution was evaporated carefully over high heat (e.g., a propane burner) while swirling the solution continuously to prevent bumping until the barium sulfate has dissolved. The heat was increased until most of the excess sulfuric acid has been expelled and a fusion was obtained. The flask was cooled and a solution of 35 mL of 30% sodium sulfate and 25 mL of water was added, with swirling to mix.

Procedures

Column preparation. Ln-Resin and DGA Resin columns were obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1-2 mL/min were typically used, much faster than the 0.25 mL/min gravity flow rates typically observed. MnO_2 Resin columns were prepared by transferring 1.25g of MnO_2 resin into small rad columns (Environmental Express, Inc. Mount Pleasant, SC). A large 200 mL column reservoir (Environmental Express, Inc.) was added to each column. By using heavy duty connectors to secure the column luer tips into the vacuum box lid (PFA 5/32"x 1/4" Heavy-wall tubing, Natural, Ref P/N 00070EE, cut to 1 inch , Cole Parmer Inc., USA with inside connector tips (Andwin Scientific CEN 4000 (250-100 uL) tips), the columns were secure even using 200 mL reservoirs. Additional racks can also be fabricated and attached to the lid to secure the columns even further if desired.

Sample preconcentration. Water samples were obtained and preserved by adjustment to approximately pH 2 using nitric acid upon sample collection. For river and groundwater samples, 1 and 1.5 liter samples were analyzed. After samples were aliquoted, Ba-133 tracer was added and 0.5 mL of 1.25M calcium nitrate was added to each sample. Twenty-five milligrams of calcium was added to each sample because initial testing showed much lower recoveries for deionized water blanks than river or groundwater samples (~60% vs. ~90%). This indicated that the relatively low ionic strength of the deionized water may have adversely affected the absorption of radium and barium on the MnO_2 resin. The pH was adjusted to pH 6-7 with 6M sodium hydroxide. The MnO_2 resin columns were rinsed with~ 25 mL of deionized water to remove any loose MnO_2 on the resin prior to loading samples. Samples were loaded at a flow rate of ~15 mLs/minute. After sample loading, the column was rinsed with ~50 mL of water. The MnO_2 was dissolved from the resin substrate with 12 mL of 4M HCL-1.5% H_2O_2 into a 50 mL plastic tube. The H_2O_2 reduces Mn (IV) to Mn (II), which dissolves easily in the HCl. If Ra-228 (via Ac-228) was required, the MnO_2 strip solution was allowed to stand for >36 hours to allow Ra-228 and Th-228 to reach secular equilibrium.

Column Separation. Stacked Ln-Resin plus DGA Resin cartridges with empty luer tip columns with 12 mL reservoirs were placed on the vacuum box. This 4M HCl-1.5% H_2O_2 strip solution was loaded onto the stacked Ln Resin plus DGA Resin column at ~ 1 drop per second. The Ln Resin removes any uranium or any thorium that may present, while Ac-228 passes through. The primary concern is uranium, however, due to the low solubility of thorium in natural water samples. The load volume plus tube rinse of 5 mL of 4M HCl was passed through the column, collected and evaporated to dryness on a hotplate. Ra-226, Ra-228, and Ba-133 were not retained on either resin, while Ac-228 was retained on the DGA Resin. The Ln Resin was removed and set aside for use later in the method. The DGA Resin cartridge was rinsed with 15 mL of 4M HCl and the Ac-228 was stripped from the DGA Resin with 10 mL of 0.5M HCl. Fifty micrograms of cerium as cerium nitrate was added, along with 1 mL of concentrated hydrofluoric acid (49%). After waiting 30 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve Filter®-Eichrom Technologies) and counted by gas proportional counting. The evaporated column load solution containing Ra, Ba and Mn was redissolved in 10 mL of 0.1M HCl with 1 drop of 30 wt% H_2O_2 added, warming as needed on a hotplate. This solution was loaded onto the same Ln Resin cartridge to further remove interferences that could adversely affect alpha resolution when the Ra-226 is measured. A 5 mL beaker rinse using 0.1M HCL was also added to the Ln Resin column. By lowering the acidity to 0.1M HCL, the retention and removal of additional interferences by Ln Resin was enhanced. By using vacuum and a flow rate of ~1 drop per second, this final purification took less than 20 minutes. A barium sulfate microprecipitation was performed similar to the one described by Sill. (11) One hundred microliters of 0.70 mg Ba/mL of barium carrier and 5 mL of 30% sodium sulfate were added to each redissolved solution, and the solution was gently mixed. One hundred microliters of barium sulfate seeding suspension was added. The solutions were mixed, placed on ice for 30 minutes, filtered onto 0.1 micron 25 mm polypropylene filters and counted by alpha spectrometry.

Figure 1 shows the vacuum box apparatus and the MnO_2 Resin columns. Two boxes were used for enhanced productivity, with a capability of twelve MnO_2 Resin columns on each box. Figure 2 shows the MnO_2 being stripped from the columns along with radium and barium using 4M HCL-1.5% H_2O_2. Figure 3 shows the stacked Ln Resin plus DGA Resin cartridges on a vacuum box. A rack that holds 50 mL plastic tubes was used for the Ln Resin/DGA Resin separation, instead of the inner liner.

Apparatus

Ra-226 measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. Polycarbonate vacuum boxes with 24 positions were used. An inner liner was used to collect the large volume of water that passes through the MnO_2 Resin columns and a rack to hold 50 mL plastic tubes was used to perform the final separation steps. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box. The Ac-228 measurements were performed with gas flow proportional counters.

Results and Discussion

Table 1 shows tracer and standard recoveries for a batch of river water samples using an aliquot of 1500 mL for each sample. The average Ra-226 recovery was 104% and the average Ra-228 recovery was 104%. The average Ba-133 tracer recovery was 90.8%, however the laboratory control sample (LCS) tracer recovery was 60%. Testing showed that deionized water used for blanks and LCS samples had lower recoveries, presumably due to lower ionic strength affecting Ra/Ba absorption kinetics on MnO_2 Resin. It was found that by adding 25 mg of calcium as calcium nitrate that the absorption increased significantly. The method was modified so that 25 mg of calcium was added to blanks, LCS samples and water samples. Table 2 shows the Ba-133 tracer recoveries for the deionized water blank and spiked blank (LCS) increased to 90% and 95%

respectively. The average Ba-133 recovery for all the samples was 94%. The average Ra-226 recovery was 97.8% and the average recovery Ra-228 recovery was 100.4%. This indicates that Ba-133 and Ra isotopes track well together using this method. Because of the large sample size (1 liter) needed to meet required detection limits of 1 pCi/L for Ra-228, the alpha spectrometry measurement for Ra-226 could be performed rapidly (4 hours or less) while still achieving very low detection limits (<0.05 pCi/L Ra-226). The Ba-133 gamma pulse height analysis measurement could be done in 20 minutes (or less) per sample. The Ac-228 measurement was performed using gas flow proportional counting, using a 30 minute count. Figure 4 shows alpha spectrometry spectra of Ra-226 in a groundwater sample, with a full width half max (FWHM) peak measurement of only 81.6 Kev. Peak broadening often seen with Ra-226 alpha peaks was minimized by passing the final solution through Ln-Resin again at low acidity. Ra-226 and Ra-228 daughters are present in the spectra of the spiked sample shown (5 pCi of Ra-226 and 20 pCi Ra-228 were added), but do not interfere. This method allows the collection and purification of both Ra-226 and Ac-228 (to measure Ra-228) in a single sample preparation method. This saves time and reduces labor costs for radium analysis. The rapid collection of Ra/Ba on MnO_2 Resin at 15 mL/minute minimizes separation time (<2 hours per liter).The strong retention of DGA Resin for Ac-228 from the 4M HCL-1.5% strip solution that removes Ra/Ba from MnO_2 Resin is both rugged and convenient. Other methods that have used retention on Ln Resin out of ~0.1M HNO3 or 0.1M HCl require very precise acidity adjustment to prevent loss of Ac-228. The separation of Ac-228 on DGA from 4M HCl is very efficient, with no negative impact from the Mn^{+2} ions or other matrix components. Early testing in this study using Ln Resin at low acidity to retain Ac-228 as in other methods indicated some adverse impact of Mn^{+2} ions on Ac-228 retention. The DGA Resin, in contrast, show excellent recovery of Ac-228.

Conclusions

The new Ra-226 and Ra-228 method developed in the SRS Environmental Laboratory is rapid and easy to use for analyses of environmental water samples. The method uses MnO_2 Resin to collect radium isotopes with Ba-133 tracer, followed by a stacked Ln-Resin/DGA Resin cartridge method to separate Ac-228 and Ra-226 for measurement. This method has high tracer recoveries, effectively removes interferences and combines the sample preparation for Ra-226 and Ra-228 to minimize separation time.

Acknowledgment

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Table Captions

Table 1 Performance of Method on River Water Samples

Table 2. Performance of Method on Groundwater Samples

Figure Captions

Figure 1. Vacuum Box System with MnO_2 Resin Columns

Figure 2 Stripping of MnO_2 with Radium from Columns

Figure 3. Stacked Ln-Resin and DGA Resin for Ra-226 and Ac-228 Separation

Figure 4. Alpha Spectrometry Spectra showing Ra-226 peak

Table 1. Performance of Method on River Water Samples

	% Recovery Ba-133	%Recovery Ra-226	% Recovery Ra-228
LCS (spiked D.I. water)	60%	106.2%	108.6%
River water	108%	N/A	N/A
River water spike	95%	102.7%	110.2%
River water spike	100%	103.1%	93.7%
Avg.	90.8%	104%	104%

1.5 L sample volume

Ba-133 tracer=1040 pCi

Ra-226 spk=5.0 pCi

Ra-228 spk=20.0 pCi

Table 2. Performance of Method on Groundwater Water Samples

		% Recovery Ba-133	%Recovery Ra-226	% Recovery Ra-228
BLK (D.I. water)		90%	106.2%	108.6%
LCS (spiked D.I. water)		95%	106.2%	108.6%
Groundwater	smp	100%	N/A	N/A
Groundwater	smp	89%	102.7%	110.2%
Groundwater	smp	97%	103.1%	93.7%
Groundwater	spike	95%	103.1%	93.7%
	Avg.=	94%	97.8%	100.4%

1.0 L sample volume

Ba-133 tracer=1040 pCi

Ra-226 spk=5.0 pCi

Ra-228 spk=20.0 pCi

Figure 1 Vacuum Box System with MnO_2 Resin Columns

Figure 2 Stripping of MnO_2 with Radium from Columns

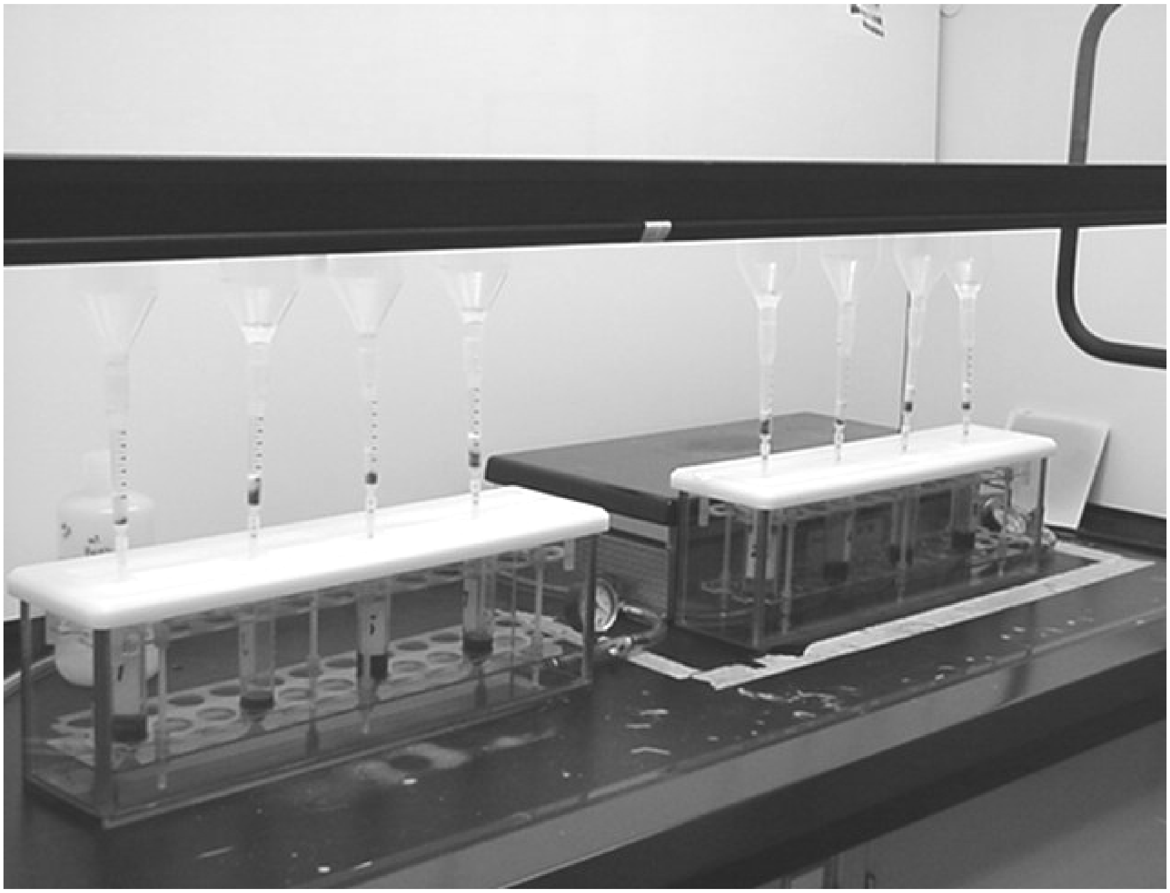

Figure 3. Stacked Ln-Resin and DGA Resin for Ra-226 and Ac-228 Separation

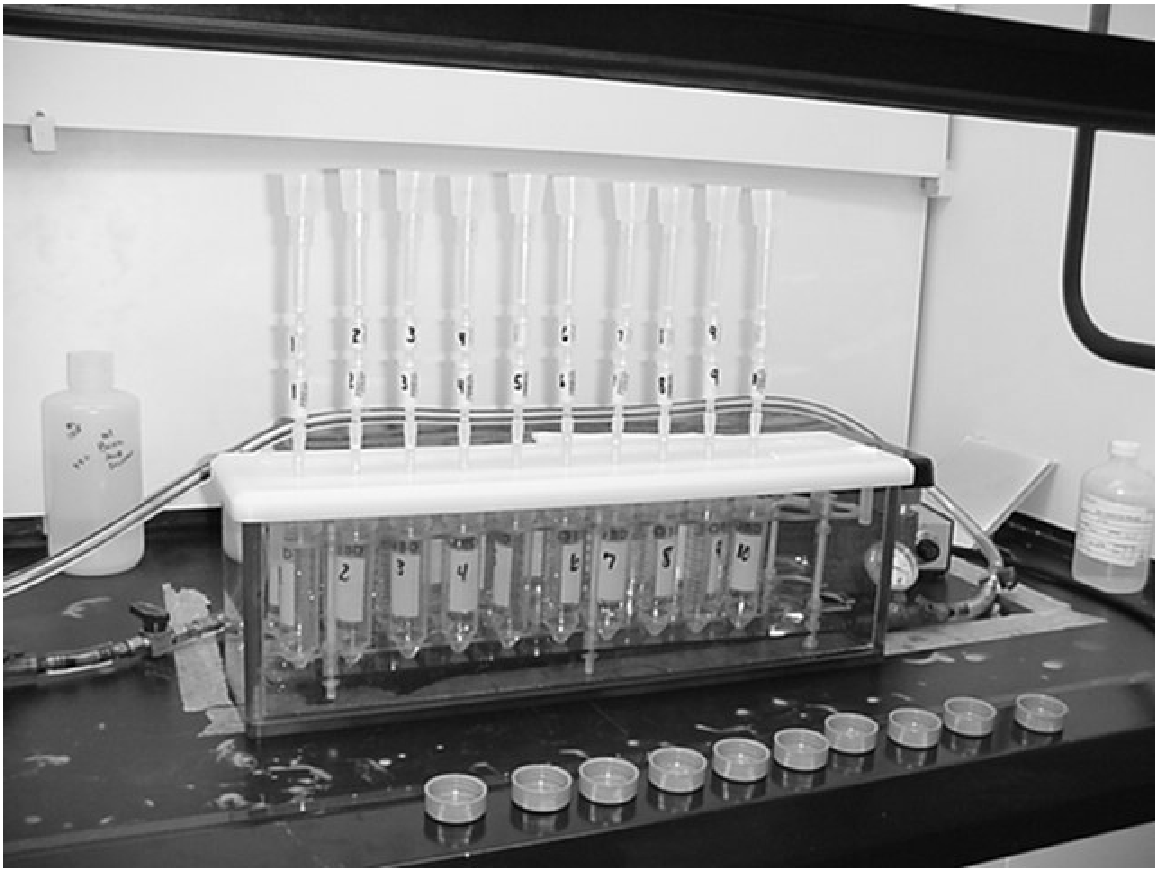
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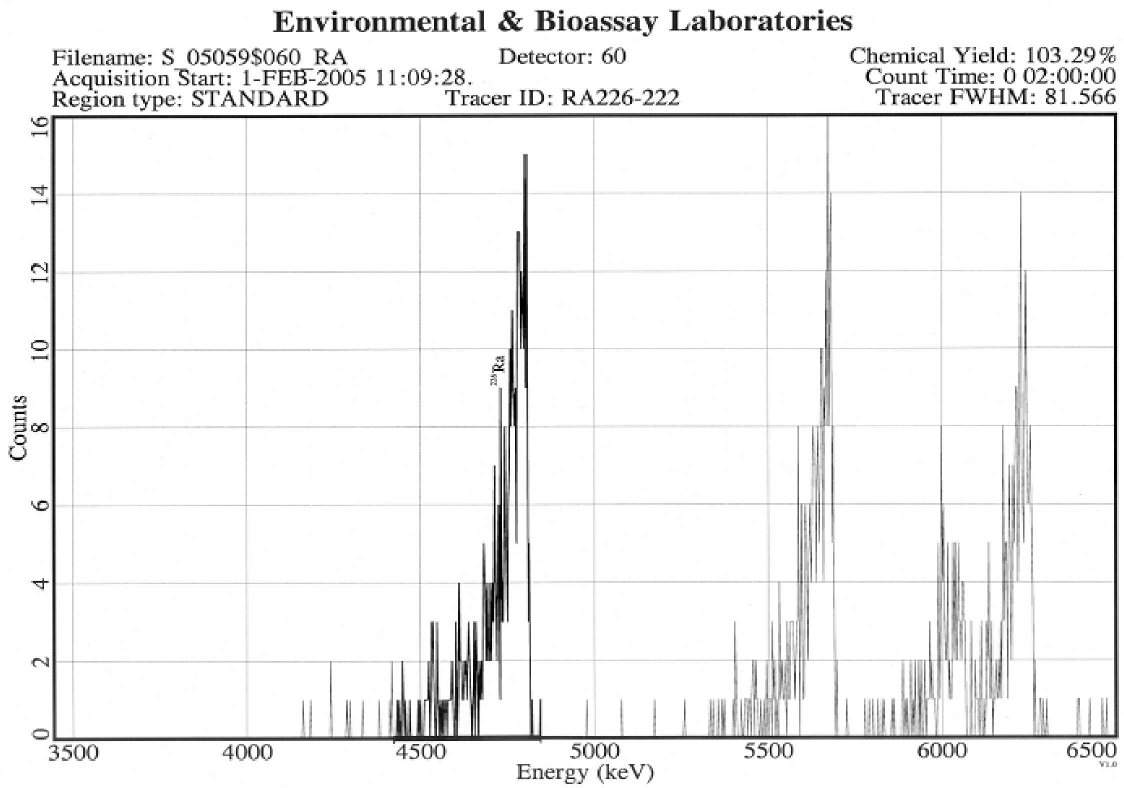
Figure 4. Alpha Spectrometry Spectra showing Ra-226 peak



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