Rapid Method to Determine Ra-226 in Steel Samples

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Abstract

The rapid measurement of ^{226}Ra in steel samples is very important in the event of a radiological emergency. ^{226}Ra ($T_{1/2}$ = 1600 y) is a natural radionuclide present in the environment and a highly toxic alpha-emitter. Due to its long life and tendency to concentrate in bones, ^{226}Ra injestion or inhalation can lead to significant committed dose to individuals. A new method for the determination of ^{226}Ra in steel samples has been developed at the Savannah River Environmental Laboratory. The new method employs a rugged acid digestion method that includes hydrofluoric acid, followed by a single precipitation step to rapidly preconcentrate the radium and remove most of the dissolved steel sample matrix. Radium is then separated using a combination of cation exchange and extraction chromatography, and ^{226}Ra is measured by alpha spectrometry. This approach has a sample preparation time of ~8 hours for steel samples , has, a very high tracer yield (>88%), and removes interferences effectively. A ^{133}Ba yield tracer is used so that samples can be counted immediately following the separation method, avoiding lengthy ingrowth times that are required in other methods.

Introduction

^{226}Ra ($T_{1/2}$ = 1600 y) is one of the most toxic of the long-lived alpha-emitters present in the environment. Due to its long half-life and tendency to concentrate in bones, injestion or inhalation of ^{226}Ra can lead to a significant committed dose to individuals. Rapid methods are needed to measure ^{226}Ra in various matrices in the event of a national radiological emergency. [1,2,3,4] 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”. [5] The ^{226}Ra isotope 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. [6]

According to Steinhäusler et al., natural radionuclides can pose a significant risk for radiological terrorism, as ^{226}Ra has been trafficked repeatedly through different countries. Furthermore, ^{210}Po has been used in a criminal act, [7] with former Russian intelligence officer Alexander Litvinenko dying in a London hospital on November 23, 2006, after he was deliberately poisoned with^{210}Po. Police discovered that those involved in this crime had spread ^{210}Po over many locations in London. [8] Because ^{226}Ra has a high specific activity relative to Uranium and many other naturally occurring radionuclides, the potential is higher for a radiological event leading to a significant committed dose from ^{226}Ra.

During a national radiological emergency, the laboratories providing analytical support will be faced with a tremendous number of samples to be analyzed very quickly. Many of the environmental samples will consist of urban matrices, building materials such as concrete, brick or asphalt. The availability of proven rapid methods will be essential to allow incident commanders to assess the scope and impact of the event. If such an emergency occurs, there will be an urgent need for rapid radiochemical analyses for building materials, including steel from building debris, to support dose mitigation and environmental clean-up. The defensibility of results is very important to maintain public trust. [9]

The application of rapid, streamlined radiochemical techniques to environmental and decommissioning samples can reduce labor costs and facilitate improved analytical efficiencies. Furthermore, reliable, high quality analyses are essential, not only following a radiological emergency, but also for routine laboratory analyses. The International Atomic Energy Agency (IAEA) AMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network administered proficiency testing for the rapid analysis of ^{226}Ra in water and phosphogypsum in 2008. The ALMERA network, established by the IAEA in 1995, is a technical collaboration of existing institutions and makes available to member states a worldwide network of analytical laboratories capable of providing reliable and timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity. Forty-nine labs from 39 member states participated in this study. Most of the laboratories used gamma spectrometry to measure ^{226}Ra by measuring the gamma ray emission of its ^{214}Bi or ^{214}Pb progeny, requiring at least a 21 day ingrowth period. This time delay would not be acceptable during a radiological emergency.

For the two water samples that contained ^{226}Ra, 43% and 31% of the lab results, respectively, were unacceptable versus IAEA test criteria. For the phosphogypsum sample, 19% of the ^{226}Ra results were unacceptable. Recommendations in this study to improve measurement quality addressed gamma calibration geometry issues, gamma emission interferences and, of particular importance the loss of the decay chain progeny ^{222}Rn due to leakage in the sample counting containers. [10]

In an emergency, where time is of the essence, long ingrowth times and poor quality results are unacceptable. A new method has been developed at the Savannah River Environmental Laboratory to measure ^{226}Ra isotopes in steel samples using alpha spectrometry. The method employs preconcentration technology that effectively manages the high iron content resulting from the dissolution of the steel sample. Rapid sample digestion and preconcentration prepare samples for column purification. The use of a ^{133}Ba yield tracer allows the direct measurement of ^{226}Ra by alpha spectrometry without waiting for progeny to ingrow, facilitating rapid analysis of samples, which will be very important in a radiological emergency. While rapid, the new method is robust, and the ^{226}Ra measurements can be performed quickly with high reliability.

Experimental

Reagents

The resins employed in this work are strong acid cation exchange resin (50W-X8, H^+ form, 200-400 mesh) and DGA Resin, Normal (N,N,N',N'-tetraoctyldiglycolamide), (available from Eichrom Technologies, Inc., Lisle, Illinois, USA, and Triskem, Bruz, France). 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.

Apparatus

The ^{226}Ra measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. The PIPS detectors have an active surface of 450 mm^2. The nominal counting efficiency for these detectors is 28-30%. The distance between the sample and detector surface is ~3 mm.

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 ^{133}Ba tracer yield for each sample. The gamma spectrometry count time was 20 minutes per sample. Canberra Genie 2000 Gamma software (version 1.3) was used to process the sample results.

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.

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 columns with reservoirs (Environmental Express, Mount Pleasant, SC, USA). DGA Resin cartridges containing 2 mL of resin were obtained from Eichrom Technologies, Inc. (Lisle, IL). Small particle size (50-100 μm) 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. For the cation exchange resin (200-400 mesh), optimum flow rates were achieved (in most cases) using gravity flow.

Sample Preparation. Figure 1 shows the flowsheet for the sample preparation for ^{226}Ra in 1 gram samples of 304 stainless steel disks ((Engineering and Information Systems, Aiken, SC, ~18% chromium, ~8% nickel). Each sample was placed in a 250 mL Teflon beaker and spiked with a ^{133}Ba tracer (~33 Bq). Twenty milliliters of 12M HCl, 5 mL 15.8M HNO_3, and 5 mL 28M HF were added to each beaker, and the samples were digested to dryness on a hot plate on medium heat to avoid any splattering. After the samples were taken to dryness, 10 mL 12M HCl, 1 mL 15.8M HNO_3, and 1 mL 28M HF were added to each beaker, and the samples were evaporated to dryness on a hot plate. Finally, 5 mL 12M HCl and 5 ml 3M HNO_3-0.25M H_3BO_3 were added to each beaker to remove fluoride. This step was found to facilitate complete removal of the sample residue from the beaker. The contents of each beaker were evaporated to dryness on a hot plate.

To dissolve the sample residue, 10 mL 0.25M HCl was added to each beaker. Each sample was warmed on a hot plate to dissolve the residue, and the dissolved sample was transferred to a 50 mL centrifuge tube. The dissolution and transfer with 10 mL 0.25M HCl were repeated two more times, warming each beaker as needed. To precipitate the Ra from the dissolved steel sample, 2 mL 1.25M calcium nitrate and 6 mL 28M HF were added to each 50 mL tube. After mixing each sample tube well, the tubes were cooled in ice bath for ~15 minutes to facilitate the complete co-precipitation of ^{133}Ba and ^{226}Ra on CaF_2. The HCl concentration was kept low (0.25M HCl) and large excess of HF was used to facilitate co precipitation of barium and radium fluoride with calcium fluoride, since BaF_2 (K_{sp} 1x10^{-6}) has a relatively high solubility product constant compared to CaF_2 (K_{sp} 5.3x10^{-9}). Each sample was centrifuged at 3500 rpm for 6 minutes and the supernate was discarded. Each sample precipitate was redissolved in 10 mL 1 M HCl-0.25M boric acid and 10 mL 1 M HCl. Each 50 mL sample tube was mixed well, warmed briefly in a hot bath and centrifuged to check for any solids. The sample liquid was transferred to a new 50 mL tube to remove any residual solids.

While this new method will need to be validated for effectiveness on other types of steel, no adverse sample matrix impact from variations in the chromium, nickel, carbon and other constituent content is expected. Iron, the key matrix component in steel, is effectively removed during the final precipitation step, while trace amounts of chromium, nickel, carbon and the other constituents of steel remaining following precipitation do not interfere with the cation exchange and DGA Resin separation methods.

Column separation for Radium-226. Figure 2 shows the column separation for radium which employs cation exchange resin for the initial sample load and rinse steps, followed by elution of ^{226}Ra through DGA Resin to remove alpha emitting interferences. The cation exchange resin column contained 5 grams of resin (200-400 mesh), although slightly more resin can be used for larger sample aliquots or for samples containing large amounts of Ca, such as steel with residual soil or concrete. The cation exchange resin 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, and gravity flow can then be used for the bulk of sample elution prior to the addition of the DGA Resin cartridges.

Prior to loading the sample, the cation resin was cleaned as follows, using gravity flow rates of 3-4 drops per second, to ensure very low blanks: 20mL deionized water, 20 mL 6M HCl, 10mL deionized water, and 10 mL 0.5M HCl. To each sample load solution, 3 mL 1.5M ascorbic acid was added to reduce Fe (III) to Fe (II) to minimize retention on the cation resin of any residual iron present. The samples were loaded at ~1 drop per second. After sample loading, the column was rinsed at ~1-2 drops/second with 25 mL 3M HCl to remove Ca^{2+}, Pb^{2+}, Bi^{3+} and UO_2^{2+} ions that may be present in the sample.

After the 3M HCl rinse, a 2 mL DGA cartridge was placed onto the bottom of each cation exchange column, and a clean labeled tube was added below each column to collect the purified eluent. To elute Ba/Ra from each cation column, 35 mL 5M HNO_3 was added to each column and eluted at ~1 drop per second. The eluents were transferred to 250 mL glass beakers, and sample tubes were rinse with 3 mL 30wt% H_2O_2. The tube rinses added to each sample beaker, and samples were quickly taken to dryness on a hotplate. The sample residues were redissolved in 10 mL 1.5M HCl with heating on a hot plate, transferred to clean 50 mL tubes. The beakers were rinsed with two 7 mL volumes of 1.5M HCl to complete transfer to the 50mL tubes, yielding purified radium fraction volumes of ~20 mL 1.5M HCl total. The purified samples are now suitable for final microprecipitation of ^{226}Ra with $BaSO_4$.

Three grams of ammonium sulfate were added to each sample, and tubes were mixed well to complete dissolution. Fifty micrograms of barium, from a 10mg/mL stock solution, was added to each sample, and and tubes wer mixed well. Five milliliters isopropanol were added to each tsample to reduce barium sulfate solubility, and tubes were mixed again. The tubes were iced for 15 minutes and periodically vortexed (beginning, middle and on removal from ice). The samples were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve- Filter-Eichrom Technologies) to collect the microprecipitate, and filters were rinsed with 3-5 mL of 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.

Results and Discussion

Table 1 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 36.4 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 36.5 mBq, with a -0.8% bias and SD (standard deviation) of 0.8 mBq. The average tracer recovery for ^{133}Ba was 95.4% ± 5.9% (SD). The high ^{133}Ba tracer recoveries and excellent results for ^{226}Ra versus known values indicate the effectiveness of the sample preparation and measurement steps. The use of calcium fluoride to coprecipitate barium fluoride and radium fluoride was successful despite the greater solubility of the Ba/Ra fluorides. The ^{226}Ra peaks for all samples show good alpha peak resolution (typically ~45keV, Figure 3). The uncertainties for the individual ^{226}Ra results in all sample sets were typically ± 7-8% (1 SD), with a 16 hour count time. Shorter alpha spectrometry measurement times may be used in a radiological emergency.

Table 2 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 73.68 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 74.9 mBq, with a 1.6% bias and SD of 3.1 mBq smp^{-1}. The average tracer recovery for ^{133}Ba was 88.8% ± 1.8% (SD).

Table 3 shows the individual results for the determination of ^{226}Ra in five 1 g steel samples spiked with 182.3 mBq ^{226}Ra using this rapid sample preparation method and measurement by gamma and alpha spectrometry. The average ^{226}Ra result was 182.9 mBq, with a -0.7% bias and SD of 4.7 mBq. The average tracer recovery for ^{133}Ba was 89.5% ± 1.8% (SD). It is not known why sample aliquot #3 has a lower ^{133}Ba yield, however it is interesting to note that without this sample aliquot the average ^{133}Ba yield is 94.5%.

The MDA (Minimum Detectable Activity) for ^{226}Ra using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie: [11]

MDA = [2.71+4.65B]/ (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 (in most cases this will be ~1) ; 0.060 = conversion from dpm to mBq.

The MDA (minimum detectable activity) for the alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. For a 1g steel aliquot, the method MDA for ^{226}Ra with a 16 hour count time is ~500 uBq g^{-1}. Shorter count times may be used in an emergency.

It should be noted this steel digestion method could be coupled with ICP-MS, however, the minimum detectable concentration is about 1 Bq g^{-1} for a 1 g steel sample, much higher than alpha spectrometry . [REF] In addition, the isobaric interference of ^{88}Sr (82.58% natural isotopic abundance) + ^{138}Ba (71.7% natural isotopic abundance), on ^{226}Ra by ICP-MS must be addressed. Both Sr and Ba can be removed using an extraction chromatographic resin containing an 18-crown-6 derivative (Sr Resin, Eichrom Technologies) as reported previously. [1]

Conclusions

A new rapid method to determine ^{226}Ra in emergency steel samples has been developed that effectively digests steel samples, such as those that may be received in a radiological emergency or from routine nuclear decommissioning. The new method features a rapid preconcentration and separation of ^{226}Ra with high chemical yields and effective removal of matrix and alpha emitting interferences. The method is rugged and very flexible, allowing several different measurement options.

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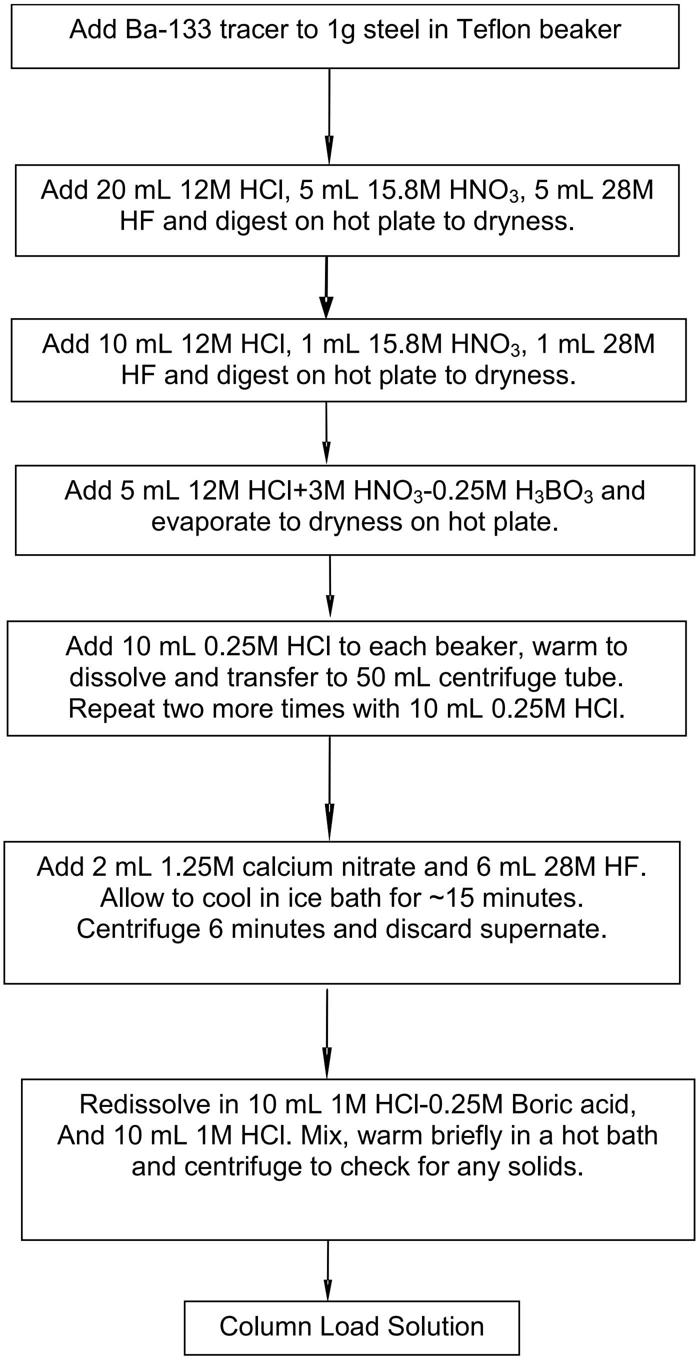
Figure 1 Steel Dissolution with ^{226}Ra Sample Preparation Method



Add Ba-133 tracer to 1g steel in Teflon beaker

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3, 5 mL 28M HF and digest on hot plate to dryness.

Add 10 mL 12M HCl, 1 mL 15.8M HNO_3, 1 mL 28M HF and digest on hot plate to dryness.

Add 5 mL 12M HCl+3M HNO_3-0.25M H_3BO_3 and evaporate to dryness on hot plate.

Add 10 mL 0.25M HCl to each beaker, warm to dissolve and transfer to 50 mL centrifuge tube. Repeat two more times with 10 mL 0.25M HCl.

Add 2 mL 1.25M calcium nitrate and 6 mL 28M HF. Allow to cool in ice bath for ~15 minutes. Centrifuge 6 minutes and discard supernate.

Redissolve in 10 mL 1M HCl-0.25M Boric acid, And 10 mL 1M HCl. Mix, warm briefly in a hot bath and centrifuge to check for any solids.

Column Load Solution

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

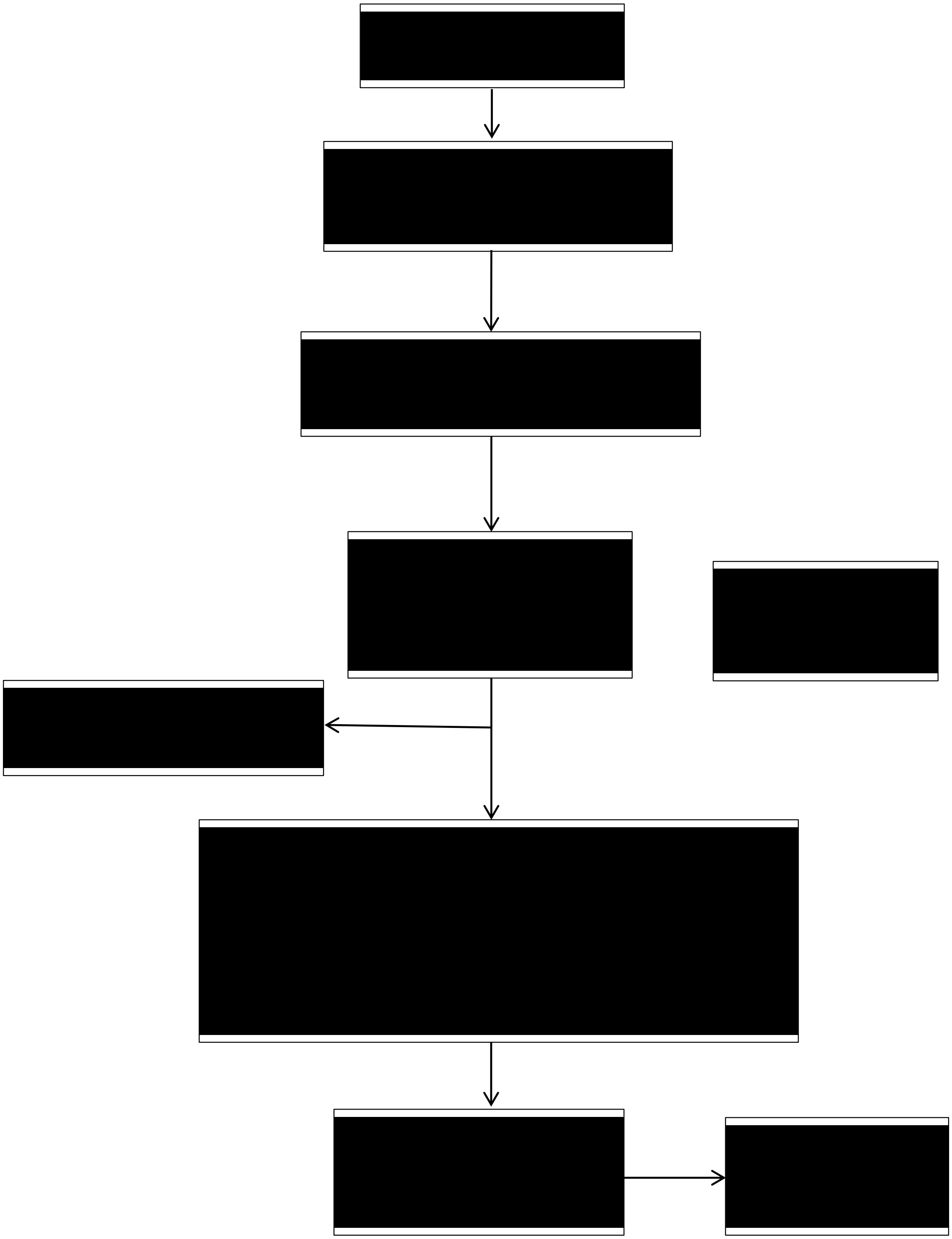


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Figure 3 Alpha Spectra for ^{226}Ra in Steel

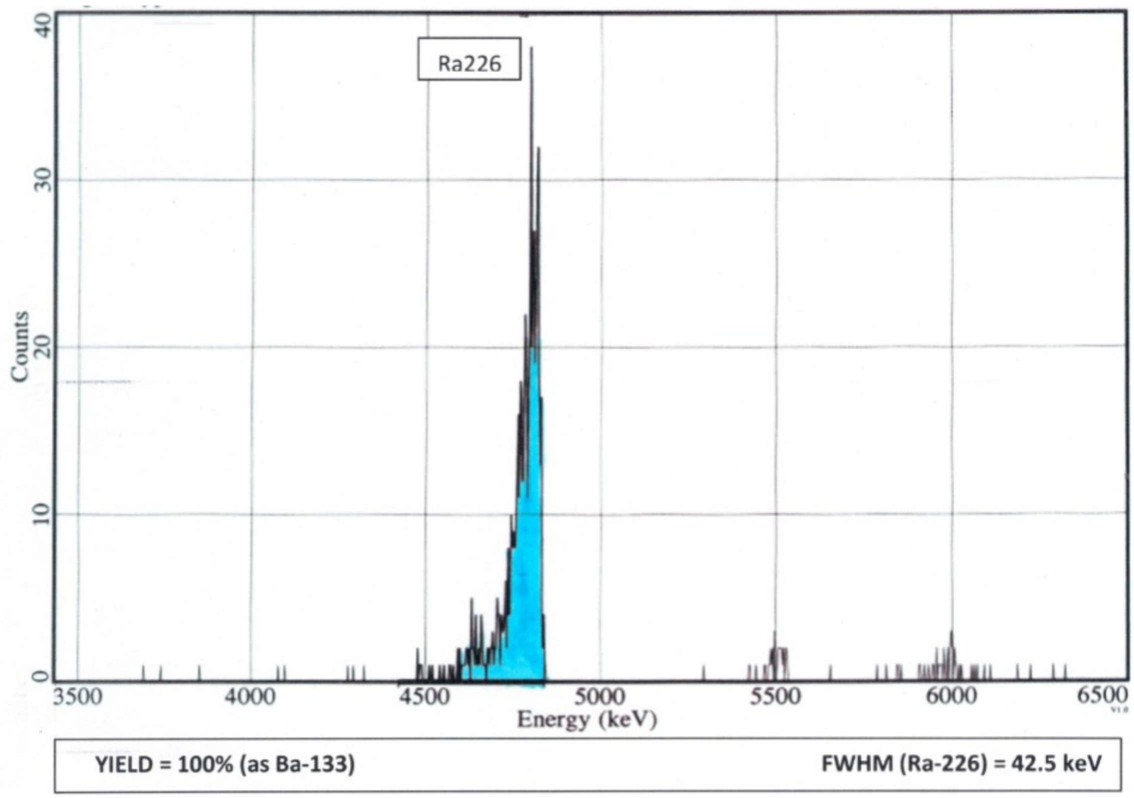
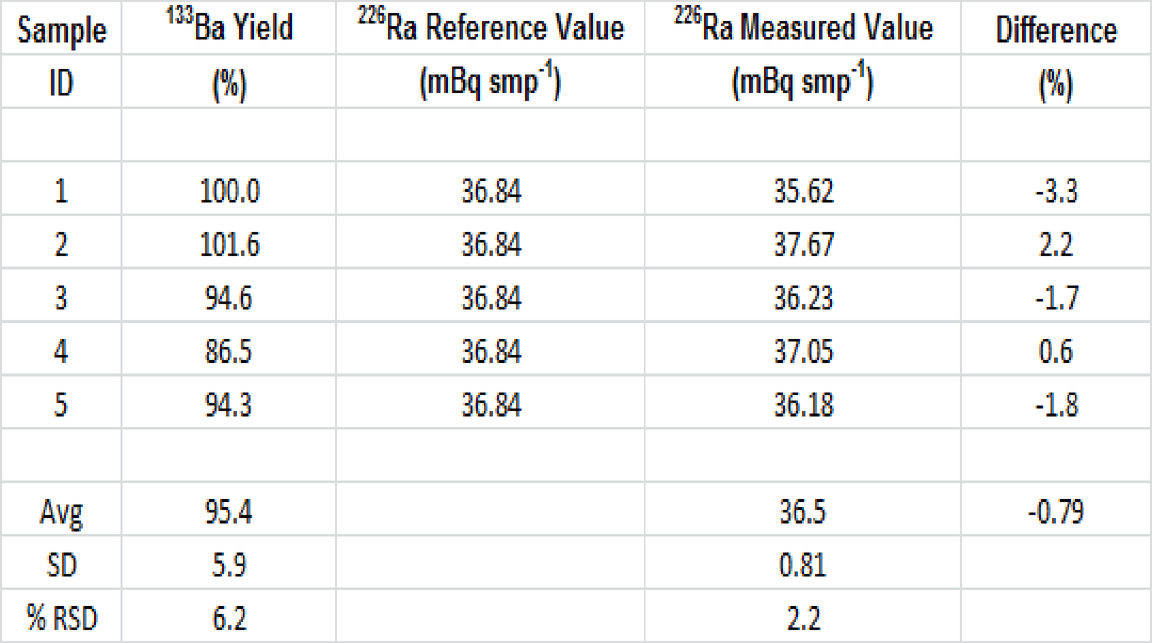
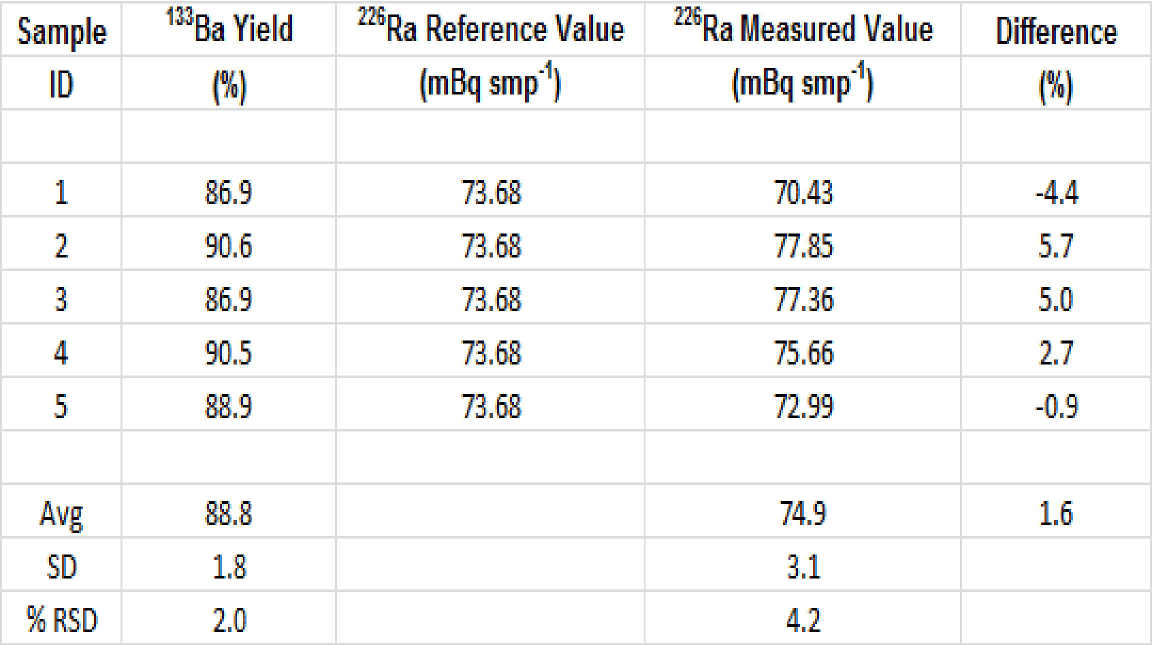


Table 1 Ra-226 Results for Spiked Steel Samples



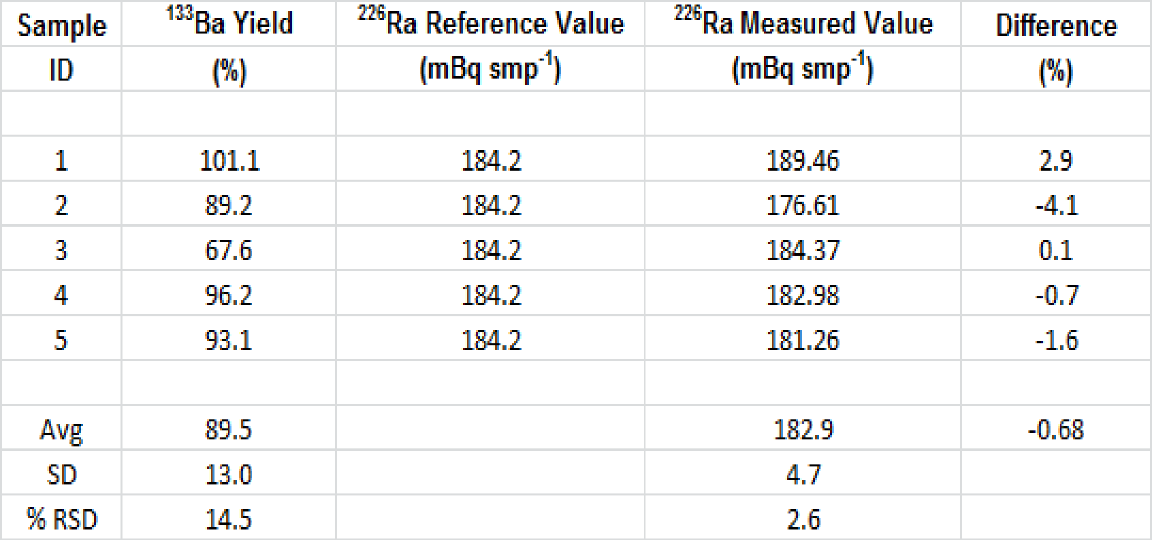
Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	100.0	36.84	35.62	-3.3
2	101.6	36.84	37.67	2.2
3	94.6	36.84	36.23	-1.7
4	86.5	36.84	37.05	0.6
5	94.3	36.84	36.18	-1.8
Avg	95.4		36.5	-0.79
SD	5.9		0.81	
% RSD	6.2		2.2	

Table 2 Ra-226 Results for Spiked Steel Samples



Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	86.9	73.68	70.43	-4.4
2	90.6	73.68	77.85	5.7
3	86.9	73.68	77.36	5.0
4	90.5	73.68	75.66	2.7
5	88.9	73.68	72.99	-0.9
Avg	88.8		74.9	1.6
SD	1.8		3.1	
% RSD	2.0		4.2	

Table 3 Ra-226 Results for Spiked Steel Samples



Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	101.1	184.2	189.46	2.9
2	89.2	184.2	176.61	-4.1
3	67.6	184.2	184.37	0.1
4	96.2	184.2	182.98	-0.7
5	93.1	184.2	181.26	-1.6
Avg	89.5		182.9	-0.68
SD	13.0		4.7	
% RSD	14.5		2.6	