



## ***TECHNICAL MEMORANDUM***

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### ***Alternate Analysis Technique for Radium-226 to Assure Compliance with Disposal Criteria at Clean Harbors Deer Trail Facility***

To: Jack Kehoe, Facility General Manager  
Clean Harbors Deer Trail

From: James M. Langsted, CHP  
CB&I Federal Services

Date: March 12, 2015

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#### ***1.0 Introduction*** \_\_\_\_\_

This document details the technical basis for using direct counting of the 186 keV photo peak from the decay of Ra-226 as a rapid counting technique for verification of meeting the Clean Harbors Deer Train (CHDT) waste acceptance criteria.

Colorado Department of Public Health and Environment (CDPHE) Radioactive Materials License Colo. 1102-01 (License Condition 10.A) requires that the summed activity of all radionuclides contained in waste materials received at the CHDT facility shall not exceed 2000 pCi/g, and additionally that the radium-226 (Ra-226) activity shall not exceed 222 pCi/g. To assure these requirements are met, CHDT requires pre-acceptance laboratory analysis of waste samples and periodic random confirmation sampling as the waste arrives at the facility (15.WAC.01).

#### ***2.0 Ra-226 Analysis by Gamma Spectroscopy of Decay Progeny*** \_\_\_\_\_

Radionuclides are analyzed by a number of acceptable test methods, specified in Table 1, Attachment D of 15.WAC.01. Ra-226 is typically analyzed by EPA Method 901.1, modified for a solid (soil) matrix. To perform this analysis, the sample is sealed in a standard-geometry container and decayed for 21 days, allowing the ingrowth of Ra-226 decay progeny to reach approximate secular equilibrium. Bismuth-214 (Bi-214) or lead-214 (Pb-214) is then quantified by gamma spectroscopy counting to determine the concentration of Ra-226 in the sample. Other gamma-emitting radionuclide concentrations are also quantified by the same gamma spectroscopy analysis.

The 21-day ingrowth requirement for this method results in a significant delay in determining the Ra-226 concentration and delays the determination if the waste meets the CHDT disposal

criteria. This delay places a burden on both the waste generator and the Deer Trail disposal facility, delaying appropriate disposition of the waste.

### **3.0 *Alternate Analysis Method***

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There are a number of techniques that provide an alternative to Ra-226 analysis by gamma spectroscopy of decay progeny. 15.WAC.01 allows the use of alternate methods of analysis with prior written approval of both Adams County and the CDPHE (Section 6.b).

A useful alternative analysis technique is to directly quantify Ra-226 by analysis of the 186.1 keV peak. The technique is evaluated in a paper written by T. Romanko (2015). The technique has a number of advantages and disadvantages discussed here. This method provides timely analysis results, in many cases is able to verify that the Ra-226 concentration of received waste meets the radioactive materials license requirements, meets the facility waste acceptance criteria, and is appropriate for placement in the CHDT disposal cell. If the result from this analysis technique is inconclusive, it is possible to continue the 21-day Ra-226 decay without further preparation of the sample and then perform gamma spectroscopy in accordance with Method 901.1.

Romanko cites the utility of this method as a relatively quick screening technique if the potentially high-biased Ra-226 result doesn't exceed a pre-defined action level, the amount of Ra-226 compared to U-235 is relatively large, and the action level is well above background levels. These criteria are met for the oil and gas field waste streams accepted at CHDT.

Ra-226 emits a 186.1 keV photon during 3.59% of its decays. All other photons emitted from Ra-226 are of insignificant quantities. Unfortunately, one of the naturally occurring isotopes of uranium (U-235) emits a photon very close in energy to the Ra-226 photon. The U-235 emission at 185.7 keV occurs in 57.2% of its decays. These energies are close enough together that modern gamma spectroscopy systems cannot resolve these two peaks and will count them together. Thus, the presence of natural uranium in the sample will bias (high) the Ra-226 result. If the result of this analysis is below the waste acceptance criteria, the result verifies that the waste is acceptable (with respect to Ra-226 concentration) for disposal. If the result is above the waste acceptance criteria, completion of the 21-day decay and Method 901.1 analysis can be completed to remove the influence of U-235 on the result and determine if the Ra-226 concentration is in excess of the waste acceptance criteria.

Detector drift at the lower (186 keV) energy and the execution of the peak search and background subtraction routines on the gamma spectrometry data do result in a greater variability in the reported result. In most cases both the Ra-226 peak and the U-235 peak are counted together and credited to Ra-226, but infrequently these variations result in

underreporting of the Ra-226 concentration. Tucker, et. al. found an average error on the 186 keV peak of 45.4%.

This alternate method will avoid the U-235 interference when applied to waste materials with less natural uranium. This is typical of oil and gas field waste materials where because of the geochemistry of these materials and the radium content of these materials is significantly higher than the uranium content. The average activity concentration of U-235 in the oil and gas field wastes that have been received at CHDT is 1.2% of the Ra-226 activity concentration. Romanko documents a study in which twenty oil field-contaminated soil samples were analyzed by both the alternate method (186 keV peak analysis) and Method 901.1 (21-day decay). The results demonstrate that alternate method safely overestimates the Ra-226 concentration in all but two low-concentration samples that are 250 times below the CHDT waste acceptance criteria. The alternate method MDC is at worst case 33 times lower than the waste acceptance criteria. An analysis of 28 filter cake samples from the oil and gas industry shows a similar utility of this technique. The danger of a false negative mistake (determining that a sample is below the waste acceptance criteria when it in fact is above the criteria), is very low.

Another disadvantage of the alternative analysis method is that the minimum detectable concentration (MDC) for this analysis method is higher than the other analysis, but it is well below the license limit of 222 pCi/g.

#### ***4.0 Evaluation of Appropriateness*** \_\_\_\_\_

An evaluation of this alternate technique has been performed using data from the oil and gas field waste streams that have been accepted at CHDT. The interference from the U-235 emissions has been considered and demonstrates that that this will not be a concern.

The average Ra-226 concentration results, routinely measured by gamma spectroscopy using 21-day decay and the total uranium results measured by the submission of samples to an outside radiochemistry laboratory were evaluated. These averages include the pre-acceptance samples and random confirmation samples routinely collected as these waste streams were accepted at the facility. The results are shown in Table 1. The natural uranium ratio of U-238 to U-235 (99.2745% to 0.720%, by weight) was applied to estimate the concentration of U-235. The decay ratios for the U-235 and the Ra-226 186 keV photons (57.2% and 3.59%) were used to estimate the photon emission rate. It was assumed that both photons are counted at the “186 keV” count and all is attributed to the presence of Ra-226. Figure 1 shows a comparison of the estimated count, including the interference from U-235, and the Ra-226 that was measured using the 21-day decay method. In all cases, the overestimate caused by the U-235 interference is not significant at a level that would affect the determination of compliance.

Romanko indicates a Total Propagated Uncertainty (TPU) of 20% - 40% in the range of 3 - 11 pCi/g Ra-226 (111 – 407 Bq/kg) measured by this technique. There is no data that extends beyond 30 pCi/g (1100 Bq/kg), however. To maintain a reasonable margin of safety, if values in excess of 150 pCi/g are reported by this alternate method, analysis by other methods should be performed to validate the result.

## 5.0 Conclusion ---

Use of direct counting of the 186 keV photo peak from the decay of Ra-226 as a rapid analysis technique to verify that waste meets the Clean Harbors Deer Train (CHDT) waste acceptance criteria is practical for wastes originating from oil and gas fields. This alternate analysis method provides a rapid analysis method which can be followed up, if necessary, by additional analysis to gain verify the analysis performed.

## 6.0 References ---

15.WAC.01, *Radioactive Materials Acceptance*, Revision 8, Clean Harbors Deer Trail LLC, March 31, 2015.

Colo. 1102-01, Radioactive Materials License, State of Colorado, Colorado Department of Health and Environment, Amendment Number 13, December 21, 2012.

EPA 901.1, *Gamma Emitting Radionuclides in Drinking Water*, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, U.S. Environmental Protection Agency, EPA-600/4-80-032, August 1980.

Romanko, T., *<sup>226</sup>Ra: An Inter-Method Comparison*, Romanko, Terry, TestAmerica Laboratories, Inc., Paper number 15447, WM2015 Conference, March 15-19, 2015, Phoenix, Arizona, USA.

Tucker, et. al., *Comparison of Activity Determination of Radium 226 in FUSRAP Soil using Various Energy Lines*, Brian Tucker, Jough Donakowski, and David Hays, Paper number 12299, WM2012 Conference, February 26 – March 1, 2012, Phoenix, Arizona, USA.

## 7.0 Attachments ---

Romanko, T., *<sup>226</sup>Ra: An Inter-Method Comparison*, Romanko, Terry, TestAmerica Laboratories, Inc., Paper number 15447, WM2015 Conference, March 15-19, 2015, Phoenix, Arizona, USA

## Figure

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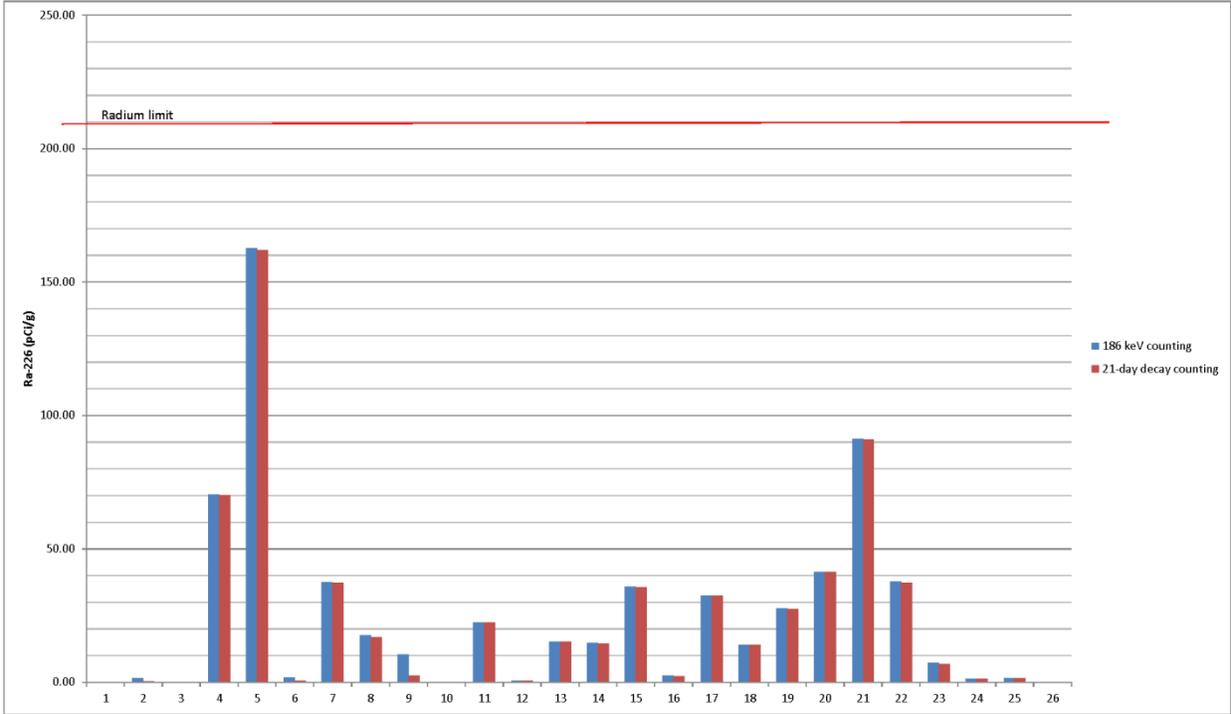


Figure 1: CHDT Waste Streams - Comparison of Analysis Methods

## **Table**

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Table 1: Estimated Ra-226 (including U-235 interference)

Waste Description	U-238	U-234	Th-230	Ra-226	Pb-210	Th-232 (Ra-228)	U-235	U-235	Ra-226	Ra-226+ U-235	Ra-226
	Avg. Conc. pCi/g	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	estimate U-235 (pCi/g)	185.7 keV (y/s)	186.1 keV (y/s)	"186" keV (y/s)	estimate (pCi/g)
Filters w/ Pb-210	0.00	0.00	0.00	0.00	177.40	0.00	0.00	0.00	0.00	0.00	0.00
Pipeline sludge and water	1.50	2.50	0.30	0.40	266.00	0.50	0.07	5.14	1.91	7.05	1.48
Filters w/ Pb-210	0.00	0.00	0.00	0.00	228.90	0.00	0.00	0.00	0.00	0.00	0.00
Oil exploration tank sludge	0.50	0.50	0.50	70.00	70.00	0.20	0.02	1.71	334.73	336.45	70.36
Sludge from oil/gas processing	1.00	1.00	1.00	162.00	162.00	1.00	0.04	3.43	774.66	778.09	162.72
Pigging Sludge With Arsenic and Lead 210 (NORM)	1.90	1.10	3.50	0.50	152.00	1.70	0.09	6.51	2.39	8.90	1.86
TENORM from Oil Processing	0.51	0.51	0.51	37.23	37.23	15.29	0.02	1.75	178.03	179.78	37.60
LBU Tank TENORM from Oil Production	1.00	1.00	1.00	17.00	17.00	0.80	0.04	3.43	81.29	84.72	17.72
NORM Sludge	11.02	25.60	0.14	2.51	480.00	1.76	0.50	37.77	12.00	49.78	10.41
NORM PPE	0.05	0.09	0.01	0.03	339.00	0.01	0.00	0.17	0.14	0.31	0.07
TENORM from Oil Processing	0.22	0.22	0.22	22.30	22.30	9.28	0.01	0.75	106.64	107.39	22.46
Spent Natural Gas Descant	0.08	0.08	0.08	0.51	46.53	0.64	0.00	0.27	2.44	2.71	0.57
TENORM Filtercake from Oil Processing	0.30	0.30	0.30	15.10	16.16	7.18	0.01	1.03	72.21	73.23	15.32
TENORM Filter Socks	0.04	0.04	0.04	14.60	14.60	10.15	0.00	0.14	69.82	69.95	14.63
NORM/TENORM Desorber Solids	0.39	0.39	0.39	35.58	35.58	13.63	0.02	1.34	170.14	171.48	35.86
TENORM Wastewater Filters	0.25	0.25	0.25	2.28	13.20	0.43	0.01	0.86	10.90	11.76	2.46
TENORM Filter Socks from Petroleum Production	0.02	0.02	0.02	32.50	32.50	19.25	0.00	0.07	155.41	155.48	32.51

Waste Description	U-238	U-234	Th-230	Ra-226	Pb-210	Th-232 (Ra-228)	U-235	U-235	Ra-226	Ra-226+ U-235	Ra-226
	Avg. Conc. pCi/g	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	Avg. Conc. (pCi/g)	estimate U-235 (pCi/g)	185.7 keV (γ/s)	186.1 keV (γ/s)	"186" keV (γ/s)	estimate (pCi/g)
TENORM filter cake from oil processing containing Ra <sup>226</sup> and Ra <sup>228</sup>	0.25	0.25	0.25	13.92	13.92	6.57	0.01	0.86	66.56	67.42	14.10
NORM impacted filter cake	0.43	0.43	0.43	27.39	27.39	12.07	0.02	1.47	130.98	132.45	27.70
NORM impacted filter socks	0.27	0.27	0.27	41.25	41.25	21.75	0.01	0.93	197.25	198.18	41.44
NORM/TENORM waste from drilling mud solidification; contains Ra <sup>226</sup>	0.16	0.16	0.16	91.00	91.00	22.20	0.01	0.55	435.15	435.70	91.11
Desorber Solids	0.45	0.45	0.45	37.35	37.35	11.50	0.02	1.54	178.60	180.15	37.67
Desorber Solids	0.83	0.83	0.83	6.75	6.75	2.85	0.04	2.85	32.28	35.12	7.34
NORM filter socks	0.00	0.00	0.00	1.26	5.16	1.06	0.00	0.00	6.03	6.03	1.26
NORM Filter Socks	0.11	0.11	0.11	1.43	1.43	1.23	0.00	0.38	6.84	7.22	1.51

## **Attachment**

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## **Ra-226: An Inter-Method Comparison - 15447**

Terry Romanko  
TestAmerica Laboratories, Inc.  
13715 Rider Trail North, Earth City, MO 63045

### **ABSTRACT**

Radium is an element which can be found naturally at low levels in the environment (water, rock, soil) as well as due to impact from man. It is known to cause cancer, primarily through ingestion and inhalation, and is considered one of the main radioactive environmental concerns. Sources of ingestion include food and drinking water, while sources of inhalation include emissions from the burning of coal or other fuels as well as dust generated from the uranium or phosphate mining industries. Radium is generally present in relatively low levels in the environment, but certain geographic formations containing elevated concentrations of radium exist throughout the world. In addition, there are sites which are considered contaminated by prior industrial activity.

Radium's most prevalent isotopes are Ra-224, Ra-226, and Ra-228. Ra-226, a member of the U-238 decay series with a half-life of 1600 years, is the most common radium isotope. Several methods exist for analysis of this isotope, some targeting measurement of this radionuclide's alpha emission (or those of its decay progeny), others focused on the accompanying gamma-ray emissions. The choice of analytical method to utilize is dependent upon various factors. The purpose of this discussion is to identify various methods, highlighting strengths and weaknesses of each to assist in determining the most advantageous method to utilize, and to compare results obtained from each method.

### **INTRODUCTION**

The most often requested radium isotope, Ra-226, appears in a variety of different projects. Whether the sample matrix is drinking water, groundwater, produced water, soil, sediment, drill cuttings, or waste the main analysis goal is typically to determine whether Ra-226 exists at or above a defined action limit or concentration. In many instances, the actual concentration is of importance (e.g. to help determine disposal, treatment or cleanup options).

While Ra-226 is primarily an alpha-emitting nuclide (94.45% branching ratio [BR] at 4784.4 keV, 5.55% BR at 4601.1 keV, and several very minor emissions), it does exhibit one gamma-ray of note (3.5% BR at 186.1 keV). Several methods exist for the determination of Ra-226, incorporating differing separation techniques and measurement instrumentation. The majority of analyses concentrate on the measurement of the alpha-particle emissions using gas-flow proportional counting (GFPC), Lucas cell counting, or alpha spectrometry (AS). In addition, several gamma spectrometry (GS) approaches may be utilized. While there are several other options [1], this paper will focus on the most commonly used methodology along with a laboratory-specific procedure.

Several compendial methods exploit the similarity in the chemistry of radium with that of barium to separate radium from the bulk sample. Such methods include EPA 903.0 (SW846 9315, SM 7500 Ra-B, ASTM D2460-90, and EPA Ra-03 employ the same approach) and EPA 903.1 (SM 7500 Ra-C, EPA Ra-04, ASTM D3454-91, and DOE Ra-05 employ the same approach). For this discussion we will focus on EPA methods 903.0 and 903.1, although the other methods listed are essentially equivalent. The laboratory-specific procedure also capitalizes, to a lesser extent, on this chemistry.

### **EPA 903.0 (GFPC)**

The Summary of Method section of EPA 903.0 states the following: “The radium in the drinking water sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Citric acid is added to the drinking water sample to assure that complete interchange occurs before the first precipitation step. The final BaSO<sub>4</sub> precipitate which includes Ra-226, Ra-224 and Ra-223 is alpha counted to determine the total disintegration rate of the radium isotopes.” The alpha count is typically performed by GFPC. Note that as this method will include several alpha-emitting isotopes of radium (intended as a screening technique for Ra-226), the procedure is aptly titled “Alpha-Emitting Radium Isotopes in Drinking Water” and results obtained could be considered as potentially high-biased Ra-226. If the total alpha-emitting radium result is less than the action level, one knows the Ra-226 result also has to be lower than this level. The advantage to this is that no waiting time is needed, thus a 3-day turnaround time (TAT) is possible, although 14 days would be more standard for this method. The laboratory reports results from this method as Total Alpha Radium (or TAR)



GFPC Instrumentation

TestAmerica’s St. Louis laboratory utilizes a modification to this method to report results as Ra-226. The method mentions Ra-226, Ra-224, and Ra-223 as the alpha-emitting radium isotopes that may be present. Ra-223 (a daughter of Th-227 with a half-life of 11.4 days) is not normally present in environmental samples, although it might be found at isolated sites (mainly former uranium enrichment or radiopharmaceutical sites). Ra-224 is a short-lived (87.8 hours) daughter in the Th-232 decay chain. As it is short-lived, after the initial radium separation/coprecipitation time is allowed for the Ra-224 to decay out of the sample. Waiting 14 days allows for 93% of any Ra-224 present to decay out, while 21 days allows for 98% to decay out. The laboratory can report Ra-226 using 903.0, with a decay/waiting period of 14 or 21 days (depending upon client need/confidence). The 903.0 methodology provides one of the lowest cost/analysis of the available methods.

### **EPA 903.1 (Lucas Cell Counting)**

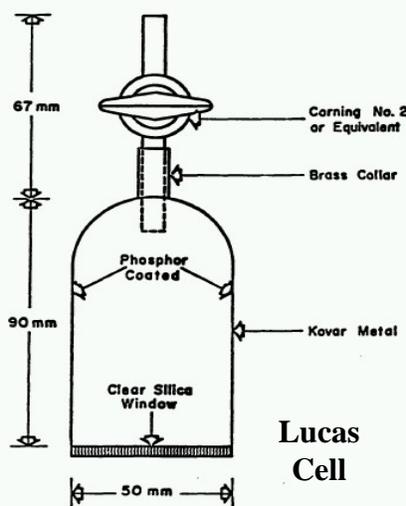
The Summary of Method section of EPA 903.1 states: “The Ra-226 in the drinking water sample is concentrated and separated by coprecipitation on barium sulfate. The precipitate is dissolved in EDTA reagent, placed in a sealed bubbler and stored for ingrowth of Rn-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived Rn-222 daughters are in equilibrium with the parent (4h), the scintillation cell is counted for alpha activity.” This technique is

commonly referred to as radon emanation. As only Ra-226 yields Rn-222 and progeny that have suitable characteristics for detection by such an emanation technique, this procedure is considered specific for Ra-226.

As can be seen from the method summaries, EPA 903.0 and 903.1 were designed for drinking water. These and other comparable methods listed find application to other liquid matrices such as groundwater or wastewater. In addition, laboratories often utilize these methods for solid matrices (e.g. soil, waste, filters, wipes) after solubilizing the radium in the sample by means of acid digestion or total dissolution.

### Lab-Specific Method (AS)

In the laboratory-specific method, radium isotopes are initially separated from the sample matrix by coprecipitation with calcium carbonate. The radium is further purified using cation-exchange and extraction chromatography resins. The final eluant containing the radium is coprecipitated with a small, controlled amount of barium as the sulfate and collected on a 0.1 micron filter. Radiometric yield is determined by alpha spectrometry (AS) of traced Ra-225 (inferred from the At-217 daughter) during the analysis count along with the Ra-226 and Ra-224 (inferred from the Po-216 or Po-212 daughter).



AS Chambers

All of the aforementioned methods (EPA 903.0, 903.1, and lab-specific) are susceptible to potential matrix issues. For example, liquid samples from the hydrofracture process, whether hydrofracture fluid, flowback water, or produced water present challenges to the traditional water chemistry methods for radiochemical analysis. The high total dissolved solids (TDS) matrix creates substantial competition in the coprecipitation and chromatography chemical separations. Secondly, the high solids content exceeds some of the method-specific limits (e.g. mass on the final planchet for measurement). Thirdly, some of the individual elements typically present in very elevated amounts (e.g. Group II alkaline earth metals Ca, Sr, Ba) directly interfere with the chemistry. Matrix issues can also be experienced for solid matrices for similar reasons.

If there is stable barium native in the samples, it will add to the mass of the barium sulfate that is formed, thus biasing the apparent chemical recovery high. This will result in a low bias to the sample results. For typical water samples, barium is not normally observed in quantities significant enough to bias the recovery. Where the recovery of barium is elevated outside QC limits (>110%) for a water sample, an ICP or ICP-MS metals analysis should be run to determine the native barium and correct the recovery accordingly. All soil samples should be analyzed for native barium. Even with native analysis performed, recoveries often remain elevated due to other interferences (e.g. elevated native strontium content) which cannot be directly/easily corrected.

To alleviate such interferences, laboratories often analyze smaller aliquots to reduce the matrix effect. However, because the interference is often so great, substantially lower aliquots would need to be used, leading to elevated minimum detectable concentration (MDC) and frequently also not completely eliminating all the interference issues. Other means for determining the chemical recovery (e.g. Ba-133 tracer for 903.0 and 903.1 and Ra-225 tracer for the lab procedure) may provide relief for the recovery issue. However, they may not eliminate other problems (e.g. large amount of mass on planchet or column over-loading). EPA method 903.1 has the greatest tolerance for sample barium content and other such issues when using Ba-133 tracer.

### **EPA 901.1 (GS)**

One cost-effective approach for samples known or suspected to contain high levels of interferences (e.g. hydrofracture projects) has been to perform gamma spectrometry (GS) (e.g. EPA 901.1) for Ra-226 on water samples, unless it is specifically known the samples are “clean” (e.g. a neighboring water well the client is testing as baseline). While the MDC by GS is much higher (~1 Bq/L) than by the drinking water methods (<0.037 Bq/L), GS avoids the chemistry issues of the 903.0/904.0 (Ra-228) methodology. And, given the high levels of activity seen in most of the samples (will vary based upon shale play, but well above 37 Bq/L in Marcellus Shale), it turns out the elevated MDC does not impact the data usability.

Ra-226 by GS is typically determined by inference from daughters (e.g. Bi-214) after sealing the sample in an appropriate counting geometry/container and waiting 21 days to allow the Ra-226 decay chain through Rn-222 to reach secular equilibrium. Such an approach is considered to be the most reliable and representative means for establishing the true Ra-226 concentration in the sample by GS. The ingrowth method is typically employed because Ra-226 analysis/quantitation by GS using its own 186.1 keV gamma-ray emission is subject to interference and potential high bias due to the 185.7 keV U-235 gamma ray. Compounding this issue is the relative peak abundances: ~3% for Ra-226 vs ~54% for U-235. This means that one count from U-235 can be mistaken as the equivalent of 18 counts of Ra-226. Experience also suggests gamma spectrometry software does not consistently assign accurate peak areas to Ra-226 (186.1 keV) and U-235 (185.7 keV), with the problem compounded by even slight drift of the instrumentation. So, while it would be expected that the 186.1 keV Ra-226 peak would normally produce a potential high bias in the presence of U-235, the laboratory has infrequently seen the Ra-226 peak area to be under-reported.



GS Instrumentation

Use of the 186 keV peak approach for background-level determination of Ra-226 in soil samples is generally not advised, as uranium is found at some level in nearly every soil type. Further, use of the 186 keV peak produces a MDC approximately 3-10 times higher than that using the Bi-214 inference approach. And, use of gamma spectrometry for analysis of Ra-226 in water samples is not normally recommended, even with the 21-day ingrowth approach, as the achievable MDC is generally too high to be of use (>1 Bq/L).

Employing the 186 keV peak, which allows for a screening method that is able to be performed relatively quickly to determine if the potentially high-biased Ra-226 doesn't exceed a predefined action level, may be warranted when:

- It is known that U-235 is not expected to be present in the sample,
- The amount of Ra-226 compared to U-235 is relatively large, or
- An action level well above background levels is targeted.

The 186 keV peak approach has been used successfully in water samples (e.g. hydrofracture flowback/produce water) for which uranium is not expected to be present in any significant amount (uranium does not normally follow the matrix) and in which the Ra-226 activity is relatively high (many hydrofracture waters exhibit Ra-226 concentrations well above the elevated MDC produced using the 186 keV peak). This approach also lends itself to verification that waste material falls below a regulatory screening limit. Thus, while the 21-day ingrowth approach is the most reliable and representative means for establishing the true Ra-226 concentration in the sample, the 186 keV approach may provide data appropriate for other uses. In such cases the data user should confirm to the laboratory their awareness of the limitations using the 186 keV peak and the approach used should be noted in the report case narrative.

Another approach is the use of an "interim" count interval (e.g. 10-day ingrowth). Results reported based upon the Bi-214 daughter with anything shorter than 21-day ingrowth are potentially biased low due to the fact the decay chain may not have reached secular equilibrium. The shorter the ingrowth, the greater the potential bias. Rn-222 is gaseous by nature, and therefore mobile/potentially volatile in a sample matrix. There are many factors which may affect the starting equilibrium, including (but not necessarily limited to):

- Soil makeup – samples with natural barite (barium sulfate) are more likely to trap Rn-222 in the matrix than other soil types
- Moisture content
- How samples are handled/collected in the field – the more the sample is disturbed, the more likely Rn-222 is to be released from the matrix
- How long samples sit in the collection container before being shipped to the laboratory for analysis
- How samples are handled at the laboratory (for example, whether samples are dried/disaggregated before placing in a geometry to count). Less Rn-222 loss is likely for samples analyzed "as-received" with reduced handling.

It is possible to apply a correction factor based upon the amount of ingrowth from sample preparation to analysis. However, to accurately apply such an ingrowth correction factor to a Ra-226 result obtained by gamma spectrometry, the laboratory must know the starting equilibrium level of the Rn-222 daughter in relation to the Ra-226 parent, information neither the

lab nor the sampler is likely to possess. In the simplest scenario, for which the Bi-214 result could be divided directly by the fractional ingrowth factor, the starting Rn-222 concentration is zero. However, the only way a laboratory could ensure a zero concentration of the Rn-222 daughter would be to perform a chemical separation, which is not typical for gamma spectrometry, especially when there are other nuclides of interest. Applying an ingrowth factor directly to a sample which has some native amount of ingrowth would actually result in a high bias to the result. The shorter the ingrowth period and the higher the native Rn-222 concentration, the larger this bias would be.

One way to estimate a starting Rn-222 equilibrium factor is for the client to set up a study of the soil type(s) involved. This would require analysis of a population of a particular soil type, both at the ingrowth interval desired (e.g. 10 days) and again after equilibrium is reached (21-days). If the data user expects results for dried/disaggregated soil (as is typically applied to ensure homogeneity, etc) the samples should be handled in this way for the study. From the resultant data, an “average” ingrowth factor for the soil can be derived. Note that this probably should be performed for each different soil type at the site, as each type may exhibit a substantially different native equilibrium factor. Short of a study such as this, the laboratory cannot know what the actual starting native amount of Rn-222 may be (and thus application of an ingrowth factor would produce potentially aberrant results).

It is preferable to report Bi-214 from analyses without ingrowth as-is (as Bi-214, not Ra-226), without any corrections, and leave the assumptions and calculations to the data user. If the laboratory does report Ra-226 with no ingrowth and no adjustment for ingrowth, a statement in the case narrative should be made to document this fact and the potential low bias. Similarly, if the laboratory reports ingrowth adjusted results when the starting equilibrium is not known, a statement in the case narrative should be included to note the potential high bias. Both of these approaches (one with a potential low bias, the other a potential high bias) come with significant risk, and the data user should confirm to the laboratory their awareness of the possible bias. It is not unusual for the results to become separated from the full report (including the narrative) in the form of a spreadsheet, and the results assumed to be “actual” Ra-226 data by others.

## **DATA COMPARISON**

To illustrate potential differences in results generated by the various methodology the laboratory generated several sets of data that can be utilized to compare the previously mentioned methods. One such set includes 60 groundwater samples analyzed by both EPA 903.0 and EPA 903.1. A second set consists of 20 soil samples analyzed by each of EPA 903.0 (as both TAR and Ra-226), EPA 901.1 (using both 186 keV and 21-day ingrowth approaches), and the lab-specific alpha spectrometry methods. A third set of data contains results for 28 filter cake samples from the oil & gas industry.

### **Data Set 1 – 60 Groundwater Samples**

Groundwater samples analyzed by both EPA 903.0 and EPA 903.1 demonstrated excellent correlation between the methods. The samples were analyzed by EPA 903.0 at the St. Louis, MO facility and by EPA 903.1 at the Richland, WA facility. Neither of the two methods

exhibited a significant bias compared to the other method (24 samples exhibited higher results by 903.0, 36 by 903.1). In addition, evaluating the sample results using a common QC parameter for replicates, the replicate error ratio (RER), yielded only three samples for which the results fall significantly outside statistical similarity (RER of 1.35, 1.35, and 1.57). The RER is calculated as the absolute value of the difference in the sample results (sample and replicate) divided by the sum of the 2-sigma total propagated uncertainties (TPU). This standard convention is utilized throughout this document. Figure 1 summarizes the results in graph form.

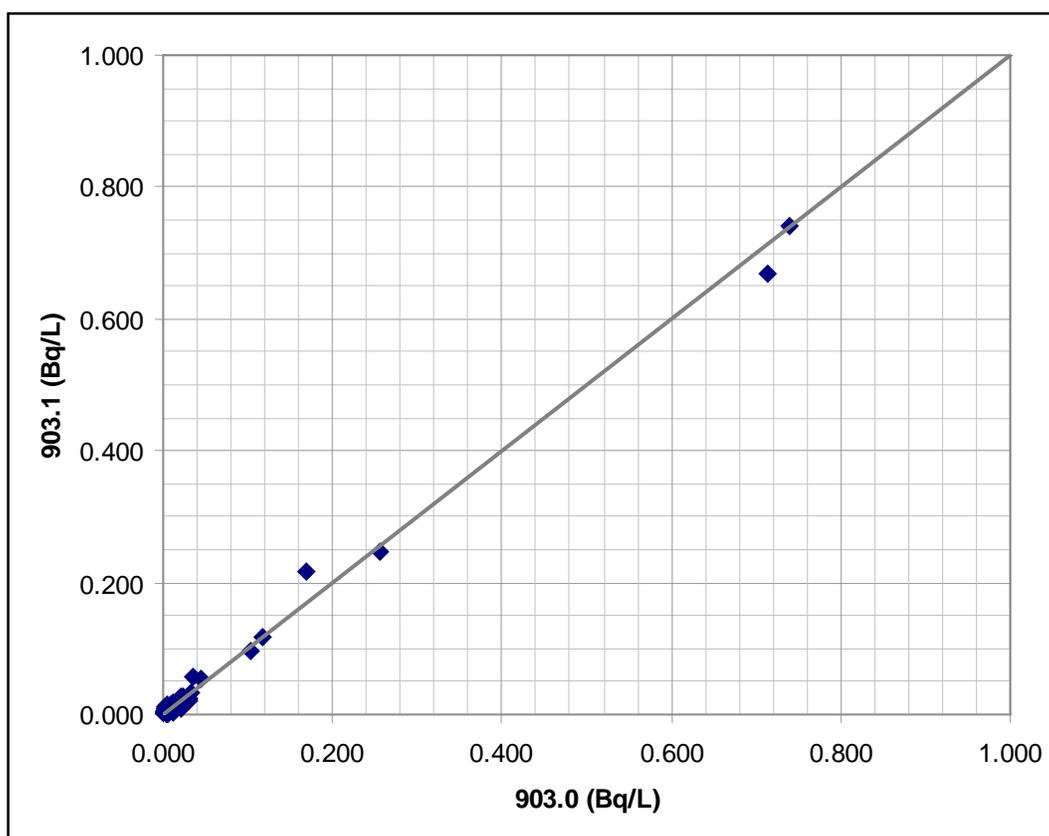


Figure 1: Comparison of Methods 903.0 vs 903.1 on groundwater samples.

### Data Set 2 – 20 Soil Samples

The soil samples analyzed represent native soil (assumed to contain some amount of native U-235) with varying amounts of precipitated barium-radium sulfate,  $Ba(Ra)SO_4$  (barite), from oil & gas produced water mixed/weathered into it. The majority of samples were selected based upon expected Ra-226 concentration  $< 370$  Bq/kg, although a few samples were chosen with higher concentrations (up to approximately 1000 Bq/kg).

The soil samples were originally counted a single time by gamma spectrometry (EPA 901.1) in a tuna can geometry with the 21-day ingrowth approach (reporting Ra-226 based upon the Bi-214 daughter) well before this study was conceived. As a separate library is utilized by the laboratory when reporting Ra-226 with 21-day ingrowth versus based upon the 186 keV peak, the spectra were reprocessed using the 186 keV library. While the 186 keV library contains the

U-235 185.7 keV peak, as stated above the Ra-226 186.1 keV peak area may include some U-235 counts. Reprocessing the spectra (as opposed to recounting the sample) eliminates potential sources of error (such as positioning of the sample, detector calibration, etc). Table I summarizes the results, presented in Bq/kg with TPU at 2 sigma. Figure 2 presents the same data in graph form with error bars.

Table I: Gamma - 186 keV vs 21-day

Sample ID	Gamma - 186 keV			Gamma - 21-day Ingrowth			>	RER
	Activity	TPU	MDC	Activity	TPU	MDC		
490-40346-2	1092	159.8	248.8	786.7	29.3	86.9	186	1.61
490-40346-4	16.0	40.5	40.6	31.2	6.4	7.1	21day	0.32
490-40346-6	64.8	32.4	34.3	28.3	5.8	6.5	186	0.95
490-40346-8	201.1	65.7	74.5	145.9	12.1	19.4	186	0.71
490-40346-14	255.6	82.9	94.2	143.2	11.6	18.8	186	1.19
490-40346-15	19.5	29.2	29.4	26.1	5.8	6.4	21day	0.19
490-40346-16	52.8	33.9	35.2	15.6	4.9	5.2	186	0.96
490-40346-20	310.5	79.0	95.8	245.7	16.3	30.3	186	0.68
490-40346-22	167.2	63.8	70.1	91.0	9.8	13.6	186	1.04
490-40346-64	269.4	72.3	86.3	175.5	12.8	22.3	186	1.10
490-40346-66	190.9	69.7	77.3	116.2	10.2	15.8	186	0.93
490-40346-70	324.6	73.3	92.6	154.4	15.0	22.0	186	1.93
490-40346-96	378.3	130.3	146.1	287.5	18.8	35.3	186	0.61
490-40346-110	144.6	48.1	54.4	59.8	10.1	11.9	186	1.45
490-40346-119	689.8	146.9	190.0	520.6	24.5	59.4	186	0.99
490-40346-124	210.2	55.6	66.6	84.1	11.5	14.4	186	1.88
490-40346-125	213.0	51.0	63.1	47.1	6.9	8.5	186	2.86
490-40346-128	91.9	43.5	46.4	47.4	7.0	8.6	186	0.88
490-40346-131	98.8	53.4	56.1	58.4	9.4	11.2	186	0.64
490-40346-135	354.7	94.4	112.9	281.9	18.5	34.6	186	0.64

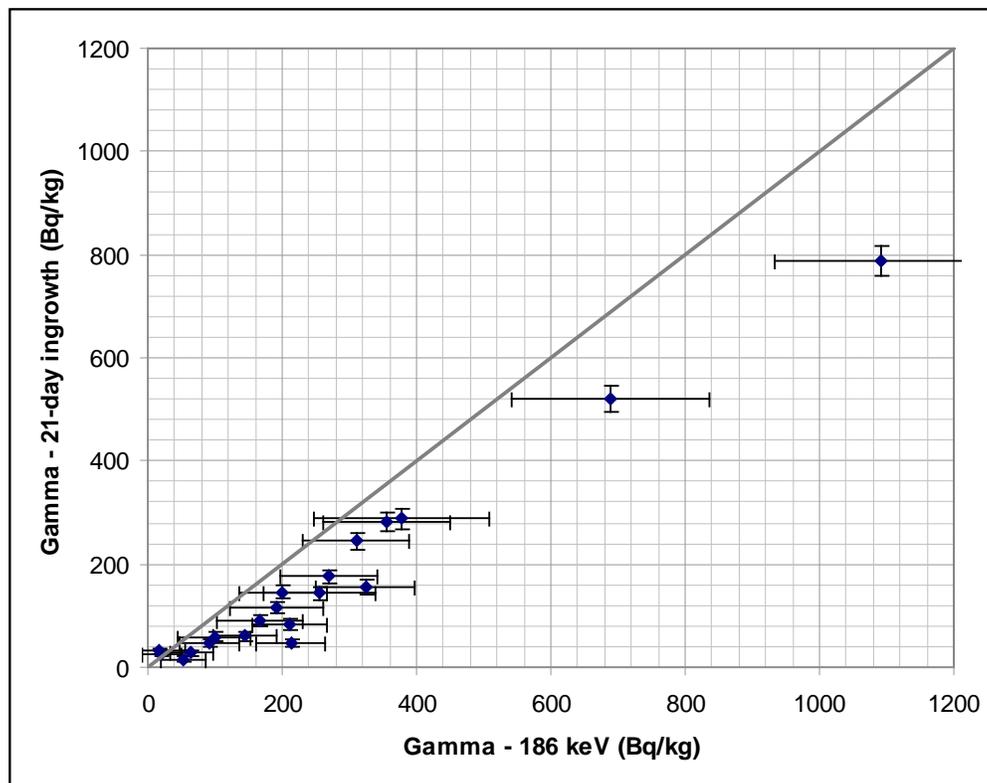


Figure 2: 20 Soil samples – Gamma Spec 186 keV vs 21-day ingrowth

As expected, the results in general demonstrate the high bias of the 186 keV approach, as all but two sample results are higher, and for those two samples the results between the 186 keV and 21-day techniques are not significantly different ( $RER \ll 1$ , thus the right-hand error bars overlap the control line). Analogous to the GFPC TAR vs 21-day (decay), if the 186 keV result is less than the action limit, it is typically assumed the 21-day ingrowth result must be as well. Note the significant difference in MDC between the two techniques, with the 186 keV producing a much higher MDC (as previously discussed).

The samples were prepared by EPA 903.0 (modified) with a 1 gram aliquot removed from the tuna can geometry using the laboratory standard dissolution technique employing mixed acids (nitric, hydrochloric, and hydrofluoric) before proceeding with the initial sulfate coprecipitation. After preparation, the samples were delivered to the count room to be alpha counted using GFPC. After this initial analysis, which represents the TAR, the planchets were set aside to allow for 21 days of decay. After this decay period, the samples were recounted resulting in the Ra-226 values. Results are summarized in Table II, presented in Bq/kg with TPU at 2 sigma. Figure 3 displays the data in graph form with error bars included.

Table II: GFPC - TAR vs 21-day

Sample ID	GFPC - TAR			GFPC - 21-day decay			>	RER
	Activity	TPU	MDC	Activity	TPU	MDC		
490-40346-2	954.6	95.5	9.14	851.0	79.6	2.62	TAR	0.59
490-40346-4	81.0	15.1	9.21	33.0	5.2	2.12	TAR	2.37
490-40346-6	37.4	9.5	7.03	10.0	2.8	2.40	TAR	2.22
490-40346-8	115.1	17.9	6.48	45.1	6.4	2.32	TAR	2.88
490-40346-14	166.9	23.2	7.10	106.2	12.2	2.42	TAR	1.71
490-40346-15	42.9	10.5	7.92	18.6	3.7	2.28	TAR	1.71
490-40346-16	35.2	9.4	7.47	8.3	2.5	2.28	TAR	2.25
490-40346-20	769.6	78.8	7.77	521.7	49.6	2.18	TAR	1.93
490-40346-22	229.8	28.9	7.55	142.1	15.4	2.62	TAR	1.98
490-40346-64	207.6	26.8	8.47	172.8	18.2	2.39	TAR	0.77
490-40346-66	136.2	19.8	6.92	112.9	12.7	2.22	TAR	0.72
490-40346-70	135.1	20.1	9.03	106.9	12.2	2.53	TAR	0.87
490-40346-96	256.4	31.4	7.22	276.8	27.6	2.27	21day	0.35
490-40346-110	64.8	12.5	6.88	41.1	5.9	2.29	TAR	1.29
490-40346-119	436.6	48.1	8.10	418.1	40.3	2.35	TAR	0.21
490-40346-124	122.8	18.6	6.66	69.6	8.7	2.55	TAR	1.95
490-40346-125	62.5	12.4	7.88	36.5	5.5	2.19	TAR	1.45
490-40346-128	81.4	14.4	6.81	37.7	5.7	2.13	TAR	2.18
490-40346-131	106.9	17.1	7.84	51.8	7.0	2.28	TAR	2.29
490-40346-135	271.6	32.8	7.47	203.5	20.9	3.26	TAR	1.27

As expected, the TAR results in general are greater than the Ra-226 values (after 21-day decay). Only one result exhibited a Ra-226 result greater than the TAR. For that sample, the RER was less than 1, suggesting the results are not statistically different. More than half of the results exhibit a significant statistical difference ( $RER \gg 1$ ). Only six of the samples would be considered acceptable replicates ( $RER < 1$ ) from a QC standpoint. However, as stated previously, if the TAR result is less than the client's action limit, the Ra-226 would be considered to be as well. Note the lower MDC for the 21-day decay data set. This is due to the ingrowth of three (3) alpha-emitting daughters in the Ra-226 decay chain contributing to a larger ingrowth factor in the denominator of the calculation equations.

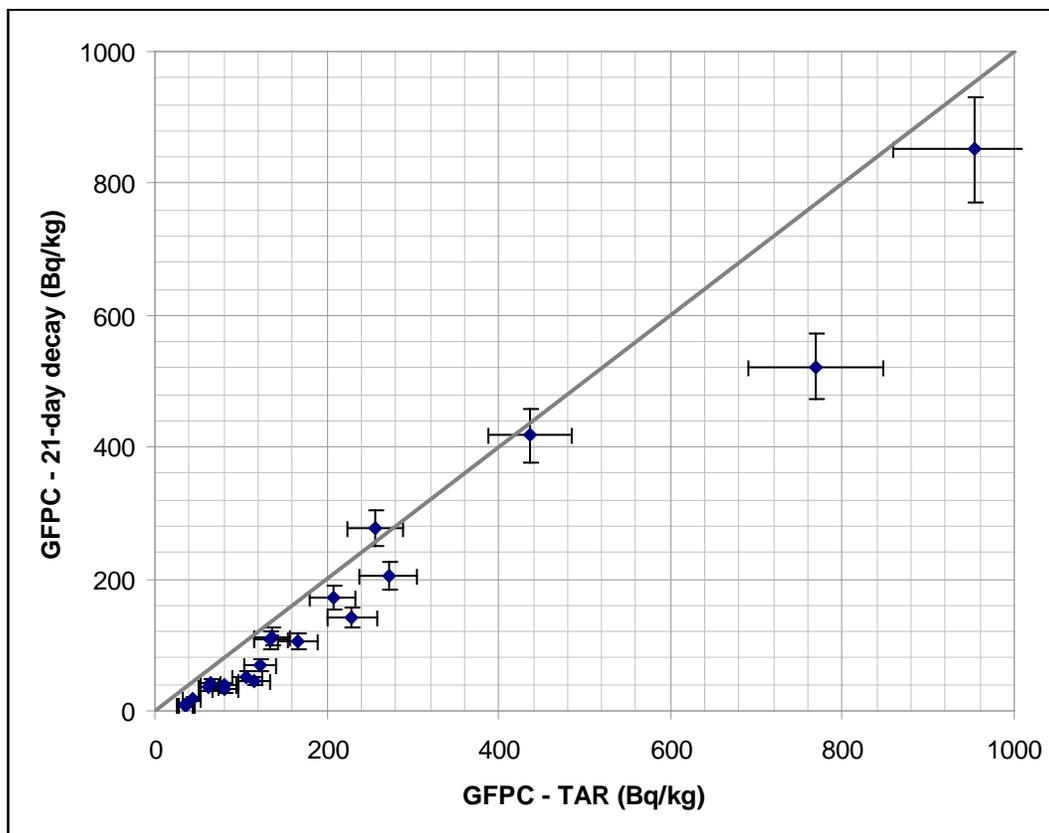


Figure 3: 20 Soil samples – GFPC TAR vs 21-day decay

The soil samples were also analyzed using the laboratory AS method via an aliquot removed from the GS tuna can. The 1 gram aliquot was put into solution employing a sodium hydroxide fusion. The data gathered from the AS method are compared in Table III to the 21-day decay (GFPC) and 21-day ingrowth (GS) results (as these are expected to best represent the true Ra-226 concentration). Results are presented in Bq/kg with TPU at 2 sigma. The same data is shown in Figure 4 in graph form with error bars. Using a RER comparison between pairs of values for each of AS:GFPC, AS:GS, and GFPC:GS we note an overall agreement between the methods (the RER for 12 of the 20 samples was <1 for all three sets). The AS:GFPC set exhibited reasonable agreement on 17 of the 20 samples. Of the three not in agreement (highlighted), two were significantly different, including one with RER = 5.65. The AS:GS data demonstrated similar consistency with 17 of the 20 samples. Of the remaining three, two displayed RER > 3. The GFPC:GS results displayed the most dissimilarity. The RER for 8 of the 20 samples exhibited significant difference. 3 of these exhibited RER similar to that of the AS:GFPC set and 3 (possibly 5) others comparable to the AS:GS set. There were no samples for which reasonable agreement did not exist for at least one of the set pairs.

Table III: Alpha Spec, GFPC 21-day, and Gamma 21-day (kBq/kg)

Sample ID	Alpha Spectrometry			GFPC - 21-day decay			Gamma - 21-day Ingrowth			AS/ GFPC	RER AS/ GS	GFPC /GS
	Act	TPU	MDC	Act	TPU	MDC	Act	TPU	MDC			
490-40346-2	921	79.9	1.13	851	79.6	2.62	787	29.3	86.9	0.44	1.23	0.59
490-40346-4	43.3	5.1	0.85	33.0	5.2	2.12	31.2	6.4	7.1	1.00	1.05	0.15
490-40346-6	27.6	3.7	0.93	10.0	2.8	2.40	28.3	5.8	6.5	2.72	0.08	2.15
490-40346-8	174	16.3	1.22	45.1	6.4	2.32	146	12.1	19.4	5.65	0.97	5.45
490-40346-14	117	11.4	0.79	106	12.2	2.42	143	11.6	18.8	0.47	1.13	1.56
490-40346-15	28.0	3.9	1.01	18.6	3.7	2.28	26.1	5.8	6.4	1.23	0.19	0.79
490-40346-16	13.8	2.5	1.25	8.3	2.5	2.28	15.6	4.9	5.2	1.10	0.25	0.98
490-40346-20	466	41.1	1.30	522	49.6	2.18	246	16.3	30.3	0.61	3.85	4.19
490-40346-22	175	16.5	1.35	142	15.4	2.62	91.0	9.8	13.6	1.02	3.18	2.02
490-40346-64	172	16.2	1.02	173	18.2	2.39	176	12.8	22.3	0.01	0.11	0.09
490-40346-66	105	10.4	1.05	113	12.7	2.22	116	10.2	15.8	0.34	0.54	0.15
490-40346-70	155	15.1	1.24	107	12.2	2.53	154	15.0	22.0	1.76	0.02	1.74
490-40346-96	330	29.5	0.23	277	27.6	2.27	287	18.8	35.3	0.93	0.88	0.23
490-40346-110	48.5	5.6	1.02	41.1	5.9	2.29	59.8	10.1	11.9	0.64	0.72	1.17
490-40346-119	444	38.9	0.88	418	40.3	2.35	521	24.5	59.4	0.33	1.21	1.58
490-40346-124	80.7	8.3	0.98	69.6	8.7	2.55	84.1	11.5	14.4	0.65	0.17	0.72
490-40346-125	48.1	5.7	1.30	36.5	5.5	2.19	47.1	6.9	8.5	1.04	0.08	0.86
490-40346-128	42.9	5.3	1.27	37.7	5.7	2.13	47.4	7.0	8.6	0.47	0.36	0.76
490-40346-131	54.4	6.0	1.11	51.8	7.0	2.28	58.4	9.4	11.2	0.20	0.26	0.40
490-40346-135	196	18.1	1.08	204	20.9	3.26	282	18.5	34.6	0.18	2.34	1.99

The author suspects some amount of non-homogeneity of these samples. In retrospect, while the samples were originally dried and disaggregated, the samples in the GS tuna can geometry (upon opening to obtain the aliquots for the AS and GFPC analyses) showed evidence for such non-homogeneity, including small rocks that were included as part of the original analysis. These small rocks were not included in the AS or GFPC aliquots, which are relatively small (1 g) in comparison to the GS aliquot (~350 g). This is a plausible explanation for the disagreement of portions of the results while there is apparent overall correspondence in results amongst the three methods.

Of possible importance to the end user of data produced from these three methods is the achievable MDC. The lowest MDC achieved was by AS, with the highest by GS. The 21-decay GFPC MDC, while much lower than that by GS, was still a factor of about 2-3 times that of AS. AS presents a couple of other advantages over the GFPC and GS methods. First is the spectral confirmation for identification (see Figure 5 for example) as well as the ability to easily determine Ra-224 (if desired). Second is the potential for a more rapid TAT – while there is a short ingrowth period necessary for the At-217 daughter of the Ra-225 tracer, results may still be available in as little as 3 days.

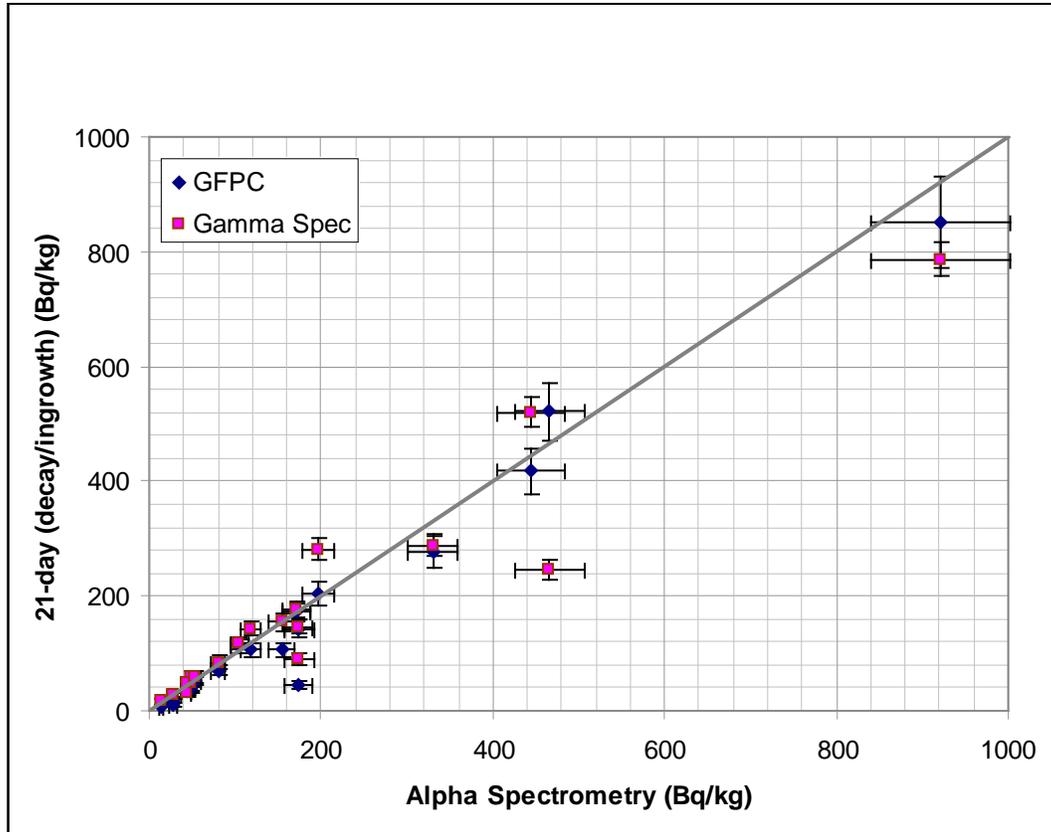


Figure 4: 20 Soil samples – Alpha Spec vs GFPC and Gamma Spec.

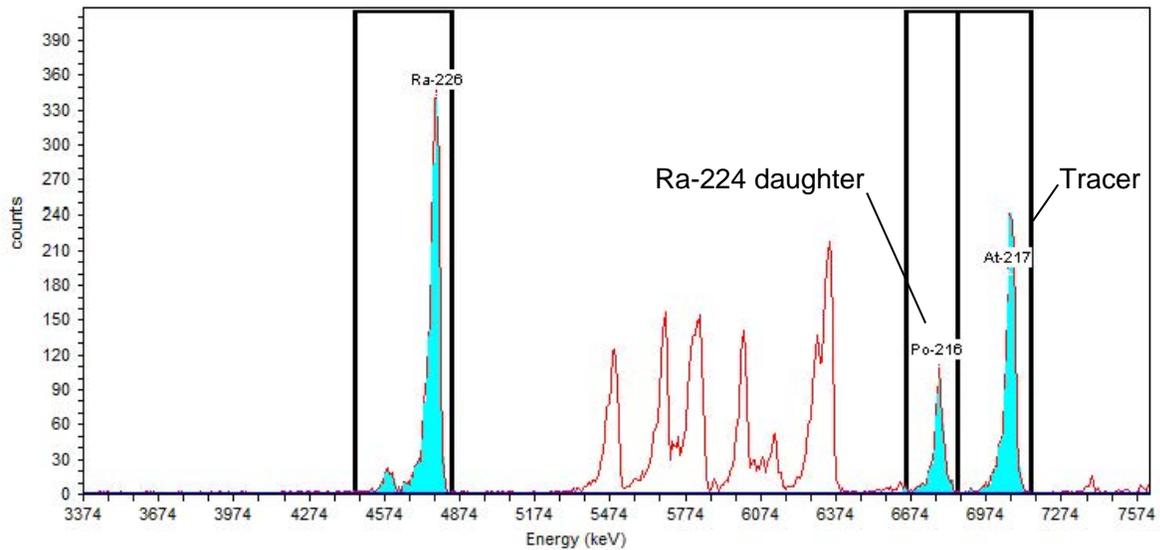


Figure 5: Alpha Spectrum from laboratory Ra-226 method

### Data Set 3 – 28 Filter Cake Samples

The third set of data, 28 filter cake samples (plus 3 sample duplicates) from the oil & gas industry is included to highlight a legitimate instance for the use of the 186 keV GS approach. These solids originate from flocculated/precipitated produced water, and are expected to contain elevated radium isotopes but no significant uranium (U-235). These samples were initially dried/disaggregated and then sealed into a tuna can geometry. The samples were counted soon after canning and processed using the 186 keV library. The samples were subsequently held for 21-day ingrowth, counted, and evaluated by means of the Bi-214 daughter. The Ra-226 activity ranged from 10 kBq/kg to 25 kBq/kg. The 4.1% average relative percent difference (RPD, which provides a better evaluation of replication at elevated activity) between the 186 keV and 21-day approaches indicates very good agreement between the methods. It is interesting to note that the 21-day ingrowth resulted in the higher average concentration. Figure 6 shows the results in graph form.

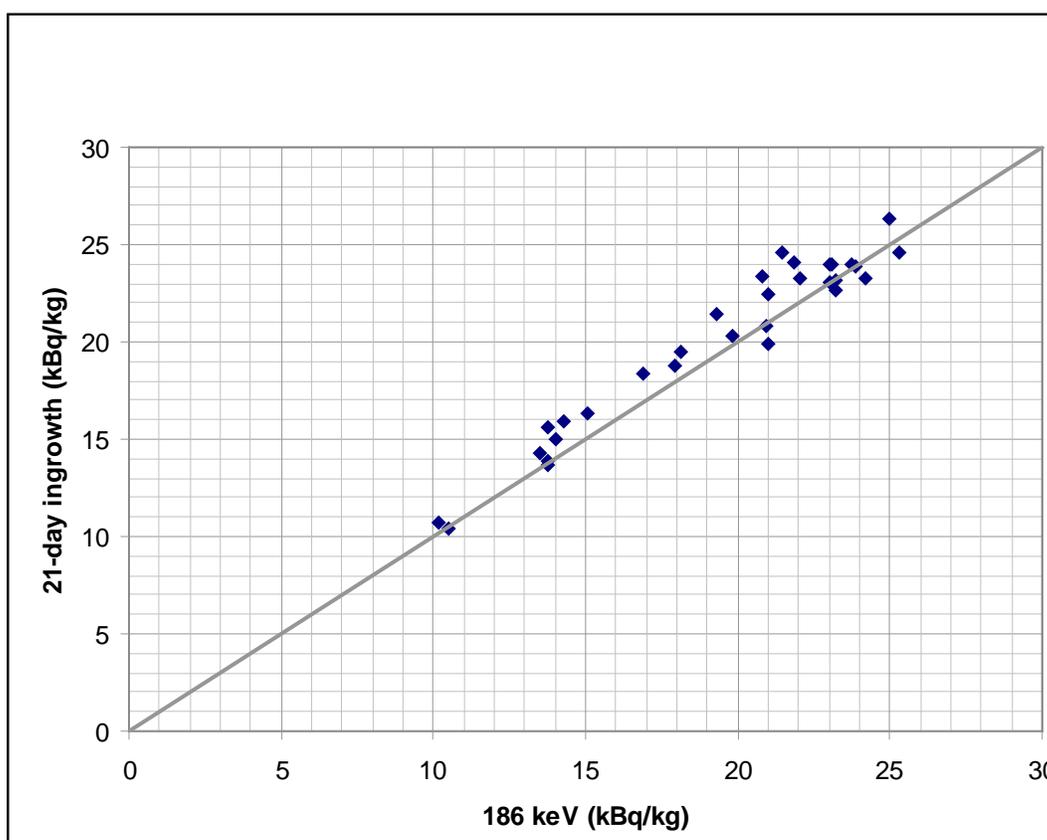


Figure 6: Filter Cake Samples – Gamma Spec 186 keV vs 21-day ingrowth

### CONCLUSION

It is apparent from the above discussion and data comparison that sufficient consideration to methodology should be made when Ra-226 analysis is a necessary part of project objectives. EPA Methods 903.0 and 903.1 have been the method of choice for many projects in the past.

However, given the current needs in a variety of different industries they may not be the best choice for all projects. Suitability of the approach for detection limit, required TAT, tolerance for bias, and even cost play a part in the decision of which method to choose.

The 21-day GFPC, 21-day GS, and AS procedures appear to produce reasonably comparable results. Approaches using GFPC and GS may offer the overall lowest cost/analysis, but AS can produce the lowest MDC. EPA 903.1 demonstrates the most tolerance to native barium and other interferences (although this benefit diminishes if Ra-228 is also required). GS offers the ability to obtain more than just Ra-226 (can report many other gamma-emitting isotopes, including Ra-228), provides some defense against non-homogeneity due to the large aliquot volume used, and eliminates the interference concerns. The TAR and 186 keV GS approaches offer the potential of rapid TAT, but at the price of a potential bias to results.

Table IV provides a quick reference for method, instrumentation, and TAT. It is strongly suggested you contact your analytical laboratory representative to discuss options in regard to your Ra-226 analysis needs to help determine the method to best fit your objectives.

Table IV: Methods, Instrumentation, and TAT

Method Reference	Analyte Reported	Instrument Type	Method Defined TAT	Standard TAT
EPA 903.0	Ra-226	Gas Flow Proportional Counter	23 days	28 days
EPA 903.0	Ra-226 as Total Alpha Radium	Gas Flow Proportional Counter	3 days	14 days
EPA 901.1	Ra-226 (from Bi-214)	Gamma Spectrometry	22 days	28 days
EPA 901.1	Ra-226 (from 186 keV)	Gamma Spectrometry	4 hours	14 days
ST-RC-0301	Ra-226	Alpha Spectrometry	3 days	14 days
EPA 903.1	Ra-226	Lucas Cell Alpha Scintillation	7 days	28 days

Method defined turnaround times do not reflect any pre-preparation techniques such as drying, disaggregating, or compositing.

## REFERENCES

1. Nelson, Andrew W.; May, Dustin; Knight, Andrew W.; Eitheim, Eric S.; Mehrhoff, Marinea; Shannon, Robert; Litman, Robert; Schultz, Michael K. Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale. *Environ. Sci. Technol. Lett.* **2014**, 1, 204-208.