Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale

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S *Supporting Information*

ABSTRACT: The rapid proliferation of horizontal drilling and hydraulic fracturing for natural gas mining has raised concerns about the potential for adverse environmental impacts. One specific concern is the radioactivity content of associated "flowback" wastewater (FBW), which is enhanced with respect to naturally occurring radium (Ra) isotopes. Thus, development and validation of effective methods for analysis of Ra in FBW are critical to appropriate regulatory and safety decision making. Recent government documents have suggested the use of EPA method 903.0 for isotopic Ra determinations. This method has been used effectively to determine Ra levels in drinking water for decades. However, analysis of FBW by this method is

questionable because of the remarkably high ionic strength and dissolved solid content observed, particularly in FBW from the Marcellus Shale region. These observations led us to investigate the utility of several common Ra analysis methods using a representative Marcellus Shale FBW sample. Methods examined included wet chemical approaches, such as EPA method 903.0, manganese dioxide (MnO_2) preconcentration, and 3M Empore RAD radium disks, and direct measurement techniques such as radon (Rn) emanation and high-purity germanium (HPGe) gamma spectroscopy. Nondestructive HPGe and emanation techniques were effective in determining Ra levels, while wet chemical techniques recovered as little as 1% of ^{226}Ra in the FBW sample studied. Our results question the reliability of wet chemical techniques for the determination of Ra content in Marcellus Shale FBW (because of the remarkably high ionic strength) and suggest that nondestructive approaches are most appropriate for these analyses. For FBW samples with a very high Ra content, large dilutions may allow the use of wet chemical techniques, but detection limit objectives must be considered.
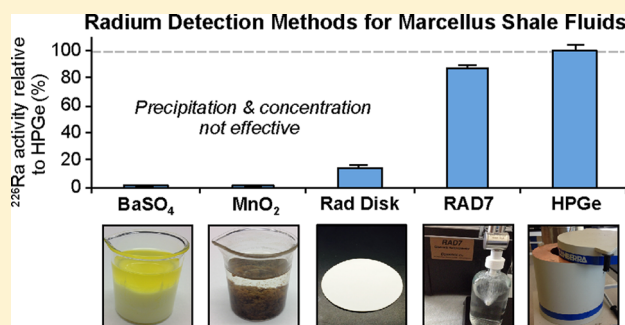
INTRODUCTION

New horizontal drilling technologies combined with hydraulic fracturing have the potential to unlock significant reserves of previously unrecoverable shale-bound natural gas around the world.[1−3] However, the rapid proliferation of these drilling techniques has sparked debate over the potential for undesirable environmental impacts. One specific concern is the radioactivity content of produced fluids and "flowback" wastewater (collectively termed FBW), which is typically enriched in naturally occurring radium (Ra) isotopes.[4,5] For example, concentrations of ^{226}Ra and ^{228}Ra in FBW from the Marcellus Shale formation in the United States (underlying New York, Pennsylvania, West Virginia, and Ohio) have been reported in peer-reviewed studies to be as high as 626 and 96 Bq/L, respectively.[4] Although these levels are not sufficient to

cause acute radiotoxicity, the large volumes and high ionic strength of FBW can overwhelm wastewater treatment facilities,[6] giving rise to radioactive contamination downstream of wastewater treatment plant discharges. For example, a recent peer-reviewed report documents ^{226}Ra contamination of approximately 200 times background in sediments downstream of a wastewater treatment plant in Pennsylvania.[7] Given the magnitude of Marcellus FBW waste (>5 billion L in 2014 alone),[8] operators and government agencies are considering

regulations to monitor wastewaters to ensure appropriate radiation and environmental protection strategies are in place.

One challenge to effective radiation and environmental protection for these activities is obtaining an accurate assessment of the radioactivity concentration of Ra isotopes in samples of FBW. Methods for quantitating isotopic Ra radioactivity in FBW have not been validated, and few peer-reviewed data sets on this topic are available. Several studies have referred to data originating from the Pennsylvania Department of Environmental Protection, which for some samples quantitated [226]Ra and [228]Ra by routine drinking water methods, specifically EPA method 903.0 and EPA method 904.0.[4,5,9] In another example, the New York State Department of Environmental Conservation proposed in 2009 (revised in 2011) that all FBW must be measured for radioactivity (before discharge) using EPA method 903.0 (alpha-emitting Ra isotopes in drinking water) and EPA method 904.0 ([228]Ra in drinking water) to quantify [226]Ra and [228]Ra (page 6-61).[10] Although wet chemical methods are robust for drinking water, because of the remarkably high ionic strength of FBW (particularly from the Marcellus Shale), the reliability of methods such as EPA method 903.0 and EPA method 904.0 is questionable for analysis of FBW. Thus, the goal of this study was to investigate the utility of several methods for analysis of Ra isotopes in a representative sample of Marcellus Shale FBW. We explored BaSO$_4$ coprecipitation (EPA method 903.0), manganese dioxide (MnO$_2$) preconcentration, a rapid 3M Empore RAD radium disk approach, analysis of [226]Ra via radon ([222]Rn) gas emanation using a portable RAD7 electronic Rn spectrometer, and high-purity germanium (HPGe) high-resolution gamma spectroscopy. Our results suggest strongly that nondestructive spectroscopic techniques are most appropriate for analysis of high-ionic strength FBW.

MATERIALS AND METHODS

General. All reagents were ACS grade or higher. The State Hygienic Laboratory at the University of Iowa complies with standards of operation and quality assurance required for accreditation by the U.S. National Environmental Laboratory Accreditation Program (NELAP). All radioactivity values are decay-corrected to 2:18 p.m. (CST) on May 15, 2013. Unless otherwise stated, all uncertainties are "standard uncertainties", corresponding to a one-uncertainty interval based on the standard deviation of multiple measurements or an estimate thereof, according to principles adhered to by international standards bodies.[11]

Flowback Wastewater Sample. The University of Iowa State Hygienic Laboratory (SHL) received a 200 L drum of Marcellus Shale FBW from northeastern Pennsylvania. The sample was extracted from a 2100 m deep, horizontally drilled well, which was hydraulically fractured with approximately 35000 m^3 of hydraulic fracturing fluid in early 2012. The sample was received May 7, 2013. Prior to radium quantitation, analysts at SHL determined the chemical composition by standard environmental techniques (Table S1 of the Supporting Information).

Surrogate Matrix. A surrogate blank matrix was prepared for quality assurance/quality control (QA/QC) analysis using reagent grade NaCl, KCl, MgCl$_2$·6H$_2$O, CaCl$_2$, SrCl$_2$·6H$_2$O, BaCl$_2$·2H$_2$O, and FeCl$_3$ in deionized water (dH$_2$O). The surrogate was prepared to match as closely as possible the FBW sample matrix based on mass spectrometry analysis (Table S1 of the Supporting Information).

Methods of Analysis Tested. *BaSO$_4$ Coprecipitation.* We attempted to use the EPA method 903.0 isotopic Ra in drinking water method of analysis. However, the addition of 20 mL of 18 M H$_2$SO$_4$, prescribed by this method, formed excessive volumes of precipitate, which rendered the approach intractable. In a further attempt to utilize the technique, we developed a modified EPA method 903.0 protocol. Briefly, three 100 mL samples of FBW, three 100 mL surrogate samples spiked with 3.7 Bq of [226]Ra, and one 100 mL surrogate blank were diluted to 1 L with dH$_2$O. EPA method 903.0 was then followed with two modifications: (1) only 0.5 mL of 1 M H$_2$SO$_4$ was added at the precipitation step (rather than the prescribed 20 mL of 18 M H$_2$SO$_4$), and (2) the Ba carrier was omitted. Counting sources were prepared according to the EPA method 903.0 protocol and were counted on a gas flow proportional counter (Berthod LB 770) for 50 min as prescribed by the method.

3M Empore RAD Radium Disks ("RAD disks"). RAD disks (3M, Eagan, MN) are wide-area (47 mm diameter) filter-based materials impregnated with a chromatographic extractant that is designed to selectively remove Ra from aqueous samples.[12] In our attempt to employ this technology for FBW analysis, three 50 mL samples of FBW were diluted to 500 mL with dH$_2$O and filtered through RAD disks, according to the manufacturer's recommendations. Disks were counted for 17 h on a Canberra HPGe detection system, calibrated to a 47 mm diameter wide-area filter geometry [Eckert and Ziegler (E&Z) 93471]. Filtrates were collected in 0.5 L Marinelli beakers and counted for 17 h using a 0.5 L liquid geometry, calibrated for energy and efficiency with an identical geometry NIST traceable standard (E&Z 93472). The radioactivity concentrations of [226]Ra in the filtrates and filters were determined by the 186 keV peak as described previously.[13,14]

Rn Emanation Measurement by RAD7. Several methods are used frequently to determine [226]Ra levels in liquid matrices based on emanation and measurement of [222]Rn, including mineral oil extraction and liquid scintillation counting and Lucas cell emanation-based gross-counting techniques. We evaluated the emanation approach using RAD7 (DURRIDGE Co., Inc., Billerica, MA), an electronic radon detector that quantifies isotopic radon activity based on measurement of short-lived alpha-emitting Rn daughters by high-resolution alpha spectrometry.[15] All materials for the RAD7 experiments were purchased from DURRIDGE and used according to the manufacturer's instructions or in consultation with the manufacturer. Briefly, glass vials (250 mL) were filled with FBW and hermetically sealed for at least 30 days to reach secular equilibrium between [226]Ra and [222]Rn. Samples were analyzed using the RAD H$_2$O accessory package, with the following minor manufacturer-recommended modification: an empty desiccant tube was inserted into the apparatus to control foaming of FBW and the relative humidity in the detector. Activities were calculated by the preprogrammed WAT250 protocol, adjusted for relative humidity with DURRIDGE Capture version 5.2.2, and decay corrected. QA/QC checks with samples of known [226]Ra activity (4, 40, and 100 Bq/L), analyzed as described above, were in agreement with the manufacturer's calibration of the detector.

MnO$_2$ Preconcentration. The method of preconcentration of Ra on MnO$_2$ has been used often for effective Ra isotopic analysis of water samples.[16−18] For our evaluation, 30 mg of KMnO$_4$ was added to 250 mL of acidified FBW and the pH was adjusted to 7−8 with 6 M ammonium hydroxide (NH$_4$OH) to form MnO$_2$. Precipitates were filtered on 0.45

μm cellulose nitrate filters (Whatman). The filtrate was transferred to 250 mL glass vials, diluted with dH_2O, and sealed for at least 30 days. Precipitates and filters were digested in concentrated HNO_3, transferred to 250 mL glass vials, neutralized with 6 M NH_4OH, and sealed for at least 30 days. Activities of ^{222}Rn were then determined by RAD7 by following the manufacturer-recommended protocol.[15] In this way, the efficiency of the MnO_2 in sequestering Ra could be assessed by the difference between the filtrate concentration and the filtered MnO_2 levels.

Gamma Spectroscopy. HPGe gamma spectrometry analysis of FBW was conducted according to routine procedures using NIST traceable standards. Briefly, HPGe gamma spectrometers were calibrated to (1) a 3 L Marinelli beaker liquid geometry (E&Z 93474), (2) a 47 mm wide-area filter geometry (E&Z CRM 93471), or (3) a 0.5 L Marinelli beaker liquid geometry (E&Z 93472), as appropriate. QA/QC included linearity and efficiency checks performed three times per week and weekly background counts. Once the bulk sample of FBW had been received, 3 L was transferred to a 3 L Marinelli beaker. Because of the settling of ultrafine particulate matter, 51 g of Bacto Agar (BD 214010) was added. The sample was heated to a low boil and then slowly cooled to form a homogeneous suspension. Gamma emissions were measured for 17 h on a 30% efficient ORTEC (Ametek, Oak Ridge, TN) HPGe, calibrated to a 3 L liquid Marinelli geometry (E&Z 93474). After 62 days, the sample was recounted on an 18% Canberra HPGe gamma detector (calibrated to E&Z 93474) to confirm ingrowth of short-lived daughters, ^{214}Pb, ^{212}Pb, and ^{214}Bi. Spectral analysis was performed using ORTEC GammaVision version 6.08 with a library that included NORM expected in FBW. Emission energies, half-lives, and their uncertainties were extracted from the National Nuclear Data Center (http://www.nndc.bnl.gov/nudat2/).[19]

RESULTS AND DISCUSSION

Chemical Matrix. Analysis of the elemental composition revealed the FBW used for this study has high concentrations of monovalent and divalent ions, solids, and transition metals (Table S1 of the Supporting Information). Briefly, concentrations of monovalent and divalent ions were as follows: 147000 mg/L Cl, 36000 mg/L Sr, 29000 mg/L Na, 13000 mg/L Ca, 9000 mg/L Ba, 850 mg/L Mg, and 160 mg/L K. The concentration of the total dissolved solids was 278000 mg/L and that of the total suspended solids 780 mg/L. The concentrations of Pb, Fe, and Mn were 1.0, 43, and 3.4 mg/L, respectively. The high concentrations of solids, Sr, and Ba are characteristic of Marcellus Shale FBW reported previously.[5,9,20]

Barium Sulfate Coprecipitation. The first method we investigated is commonly used for Ra concentration determinations in drinking water, i.e., EPA method 903.0. This method involves the addition of $BaCl_2$ and H_2SO_4 to precipitate Ra as $Ba(Ra)SO_4$. We found that following the procedure as written results in copious, unmanageable quantities of precipitate. Because of excessive precipitate formation, we were unable to use EPA method 903.0 to quantify Ra activities in samples as small as 10 mL. To determine whether a modified form of EPA method 903.0 would be useful, we reduced the quantity of H_2SO_4 by a factor of 720 and diluted the salt concentration by a factor of 10. This reduced the final precipitate to acceptable mass ranges but resulted in poor recovery of Ra. Activities of ^{226}Ra surrogate spikes were calculated to be <1% of spiked

activity. Similarly, activities of FBW were calculated to be <1% of the ^{226}Ra activity determined by HPGe. We interpret this finding as illustrating that the similar chemistry of Ra and Ba prevents the use of $Ba(Ra)SO_4$ precipitation in samples with large Ba:Ra mass ratios (nearly $1:10^9$ in this sample), as are commonly found in FBW. Thus, our data suggest that $Ba(Ra)SO_4$ coprecipitations are not appropriate for analysis of FBW in general and (in particular) for the analysis of Marcellus Shale FBW. These laboratory findings may also explain observed difficulties experienced by wastewater treatment facilities (using similar coprecipitation approaches) in removing Ra from FBW,[7] potentially leading to improved wastewater treatment strategies.

3M Empore Radium RAD Disks. RAD disks have been used successfully to concentrate Ra from aqueous environmental samples.[21,22] The use of the RAD disk technology is appealing, because the approach is rapid, with fewer wet chemical steps than $BaSO_4$ coprecipitations.[21] The manufacturer reports the disks recover >95% of Ra in samples with high concentrations of divalent cations, although a published peer-reviewed upper limit of metal concentration has not been established, to the best of our knowledge.[12] When we tested 50 mL of FBW, diluted 10-fold in dH_2O, the recovery of ^{226}Ra was $13 \pm 1\%$ ($n = 3$) of values obtained by direct measurement using HPGe. Although recovery was low, others have suggested radioactive tracers, such as ^{133}Ba or ^{225}Ra, could be used for isotope dilution-based approaches.[22,23] Nonetheless, the efficiency of the RAD disk appears to be questionable for high-ionic strength FBW, and a more thorough study is needed to establish an upper limit of ionic strength within which the technology can be reliably employed for analysis of FBW.

MnO_2 Preconcentration. Manganese dioxide is used often to preconcentrate Ra for radiochemical analysis.[16−18] However, we hypothesized the divalent-rich matrix of FBW would hinder the efficiency of the approach. To test this assertion, we performed MnO_2 preconcentration of FBW to determine if ^{226}Ra would sorb to MnO_2 or remain in solution. Results indicated that MnO_2 scavenged <1% of ^{226}Ra from the FBW (i.e., the filtrate contained >99% of the ^{226}Ra). Although preconcentration with MnO_2 is useful for certain complex matrices, high-ionic strength brine, such as that from the Dead Sea, has been reported to reduce Ra recovery on MnO_2-impregnated acrylic fibers.[24] Similarly, our results indicate that the high concentrations of divalent cations in FBW interfere with the use of MnO_2-based preconcentration for the analysis of FBW.

Rn Emanation Measurement by RAD7. RAD7 is a sturdy, portable, electronic radon detector that can be used to measure ^{222}Rn and ^{220}Rn (decay products of ^{226}Ra and ^{224}Ra, respectively) in environmental water samples in field and laboratory environments.[25−27] The system can be used to measure unsupported ^{222}Rn and ^{220}Rn levels in water, by immediate measurement, as well as ^{226}Ra and ^{224}Ra by hermetically sealing water samples and allowing sufficient time for Rn radioactivity products to reach radioactive equilibrium. When the RAD H_2O closed-loop system is used, the RAD7 can measure ^{222}Rn activities in water from <0.37 to 14800 Bq/L.[15] Measurement of ^{226}Ra in FBW via ^{222}Rn emanation is advantageous relative to wet chemical analysis techniques because Rn gas can be stripped from complex chemical matrices, allowing for sample volumes larger than and detection limits lower than those of precipitation methods. On the other hand, for analysis of the Marcellus Shale FBW sample

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described here, controlling foam produced during the Rn gas-stripping process using RAD7 was a challenge. To alleviate the problem, we inserted an empty desiccant tube between the sample vial and the filled desiccant tube. Another (related) challenge was controlling the humidity in the detector chamber, which can reduce the counting efficiency of the RAD7 device. When adjusted for humidity using the DURRIDGE Capture software and for volume introduced by the empty desiccant tube, the radioactivity level of the ^{226}Ra level in FBW observed in this study was 610 ± 10 Bq/L ($n = 3$). This estimation of ^{226}Ra may differ from HPGe values for several reasons, including the effects of brine on the solubility of Rn.[28] Additionally, modifications to the RAD7 may be necessary to reduce possible interference from dissolved gases.[29] A more rigorous examination of these parameters is ongoing in our laboratory. If analysis of large numbers of samples is required rapidly, in a high-throughput laboratory environment, mineral oil-based ^{222}Rn extraction/emanation and liquid scintillation counting and Lucas cell-based emanation techniques can be employed to improve throughput. A potential drawback of ^{226}Ra measurements by this method is the holding time for radon ingrowth. The holding time may be as short as 4 days if the sample is purged prior to being hermetically sealed; however, because sample foaming prevented complete purging, we chose to hold for 30 days to establish secular equilibrium. Thus, for samples with sufficient ^{226}Ra radioactivity content, direct measurement by HPGe gamma spectroscopy (as described below) may offer a simpler solution to achieving statistical significance in radioactivity quantitation.

HPGe Gamma Spectroscopy. HPGe gamma spectroscopy is well-established for the determination of the levels of ^{228}Ra, ^{226}Ra, and ^{224}Ra in environmental samples, with achievable detection limits depending primarily on sample size, detector efficiency, and available counting time.[30−32] Within these constraints, given that the Ra isotopic concentration of Marcellus Shale FBW is relatively high, the clear advantage of HPGe gamma spectroscopy for the analyses here is the simplicity of sample handling (i.e., no wet chemistry required; apart from the addition of agar and moderate heating, no alterations were made to the sample). Thus, high-ionic strength FBW samples can be measured directly, and samples can be stored for future analysis (if required). Radium activities observed in the representative FBW sample used for this assessment are well in excess of typical environmental levels in natural surface waters reported in this region of Pennsylvania [^{226}Ra, 670 ± 3 Bq/L; ^{228}Ra, 76 ± 1 Bq/L (Table 1)].[7] ^{228}Ra activities were determined by integration of ^{228}Ac radioactive product peaks (911 and 338 keV), with an achievable minimal detectable activity (MDA) of 0.6 Bq/L under the counting conditions employed. The ^{226}Ra value was determined on the basis of a direct measurement of the 186 keV ^{226}Ra peak, with an achievable MDA of 3 Bq/L. Although interference from ^{235}U gamma ray emission in the 186 keV region is possible,[33] preliminary analysis of natural U isotopes ^{238}U, ^{235}U, and ^{234}U by alpha spectrometry reveals activities of <0.01 Bq/L of FBW. Thus, the contribution of ^{235}U to the 186 keV region is negligible for these analyses. Very little natural U is extracted during the hydraulic fracturing process because of the insolubility of U under the reducing conditions at depth in the shale deposit. Further studies are required to develop a detailed understanding of the behavior of U in unconventional, drilling-derived solid waste and in the FBW use cycle (a topic of

Table 1. Comparison of ^{226}Ra Quantitation Methods

method	sample description	volume (L)	^{226}Ra recovery (%)	^{226}Ra (Bq/L)
BaSO$_4$ coprecipitation	surrogate spike (3.7 Bq of ^{226}Ra)	0.1	<1[b]	0.15 ± 0.03[d]
	FBW[a] and 0.5 mL of 1 M H$_2$SO$_4$	0.1	<1[b,c]	1.9 ± 0.4[d]
Empore RAD disk	FBW diluted 10-fold, RAD disk	0.05	13 ± 1	96 ± 8[d]
	FBW diluted 10-fold, supernatant	0.05	87 ± 1	642 ± 1[d]
MnO$_2$ concentration	FBW and 10 mg of Mn, precipitate	0.25	<1	0.9 ± 0.3[d]
	FBW and 10 mg of Mn, supernatant	0.25	>99	600 ± 20[d]
RAD7	FBW	0.25	91[c]	610 ± 10[d]
HPGe	FBW and Bacto Agar	3	100	670 ± 26[e]

[a]FBW, flowback water. [b]Assuming a 100% efficiency of Ba recovery. [c]Relative to the HPGe 186.2 keV peak. [d]Uncertainties are reported as the standard deviation of three counts. [e]Counting uncertainty.

current research in our laboratories). Lower radioactivity concentrations of ^{228}Ra (and decay products ^{224}Ra, ^{212}Pb, and ^{208}Tl) relative to those of ^{226}Ra (and decay products ^{214}Pb and ^{214}Bi) can be explained by a lower concentration of natural Th (^{232}Th relative to natural ^{238}U) at depth in the shale deposit. Importantly, regardless of the decay product equilibrium and/or disequilibrium associated with FBW, direct measurement of ^{226}Ra requires no holding time and can be measured directly by HPGe via the 186 keV gamma ray emission of ^{226}Ra. When possible, measurements conducted using the 186 keV peak can be confirmed by measuring ^{226}Ra decay product ingrowth after the proper holding time. The radioactive equilibrium of ^{228}Ac ($t_{1/2}$ = 6 h) with ^{228}Ra is reached in ∼36 h for these analyses. While ionic strength differences between control standards and high-ionic strength samples under analysis can contribute to inaccuracies in Ra isotopic measurements due to density differences, our analysis of surrogate FBW indicates no significant contribution.[34] Differences in the ^{226}Ra radioactivity level determined by the RAD7 emanation method may be the result of inaccuracies in humidity corrections applied, and an improved apparatus can easily be envisioned for efficient field studies by this emanation technique (a topic of ongoing research in our laboratories). Nonetheless, our results strongly suggest that wet chemical techniques (e.g., EPA method 903.0) are unlikely to be reliable for the analysis of high-ionic strength FBW, and direct measurement by emanation techniques and HPGe spectroscopy is recommended for accurate assessments. For FBW samples with a very high Ra content, large dilutions may be applied (to dilute the ionic strength) to allow the use of wet chemical techniques, but detection limit data quality objectives must be considered.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Chemical composition of flowback water (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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