

RAPID PRECONCENTRATION OF RA-226 IN HYDRAULIC FRACTURING WASTEWATER SAMPLES FOR GAMMA SPECTROMETRY ASSAY

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A new rapid method that rapidly preconcentrates Ra-226 from hydraulic fracturing wastewater samples was developed in the Savannah River Environmental Laboratory to improve the quality of Ra-226 measurements using gamma spectrometry. The method provides a lower detection limit and eliminates potential U-235 interference at the 186 keV gamma ray energy used to measure Ra-226. The rapid method provides up to 100x preconcentration of Ra-226 from this difficult sample matrix, which contains very high levels of calcium, barium, strontium, magnesium and sodium.

This approach eliminates the problems reported by Nelson et al ¹ regarding Ra-226 preconcentration and U-235 removal from fracking flowback samples. This included very low chemical yields, sample processing problems associated with high levels of dissolved solids and precipitation during direct gamma spectrometry measurements. This new method allows rapid collection of Ra-226 along with the large amounts of barium present in an easily measured, evenly deposited solid layer, with adjustments made for gamma ray attenuation at 186 keV using the Ba-133 gamma rays at 81 keV and 356 keV. Using this simple, yet effective approach, no drying and weighing to develop a mass attenuation curve for Ra-226/Ba-133 is needed.

A novel precipitation step is applied to first remove large amounts of calcium and strontium present, as well as U-235. Ba-133 tracer is used to determine chemical yield, which is typically 80-90%. The high chemical yield facilitates a low detection limit and indicates method ruggedness. The MDA for this method for a 1L sample aliquot is <20 pCi/L for a 1000 minute count using a high purity germanium (40% efficiency). This is significantly lower than the 80-100 pCi/L MDA levels typically reported for direct gamma spectrometry and/or ICP-MS methods. ^{1,2} Shorter count times may be employed for higher level samples. Up to 1.8L of fracking simulant has been tested. The sample preparation takes < 2 hours.

No time-consuming column chemistry is required. No addition of agar with heating is required to counter the precipitation of ultrafine particulate matter.¹ This method does not rely on the ingrowth of Ra-226 progeny, and therefore can be applied quickly and easily without hold times to facilitate sample throughput. A rapid method to quickly preconcentrate U/Th for the determination of U-235 and Th-228 by gamma spectrometry, or U and Th isotopes by alpha spectrometry will also be discussed.

- 1 A. Nelson et al, Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale *Environ. Sci. Technol. Lett.*, **2014**, *1* (3), pp 204–208
- 2 T. Zhang et al, Analysis of Radium-226 in High Salinity Wastewater from Unconventional Gas Extraction by Inductively Coupled Plasma-Mass Spectrometry *Environ. Sci. Technol.*, **2015**, *49* (5), pp 2969–2976