

A RAPID DETERMINATION OF RA-226 AND RA-224 USING EXTRACTION CHROMATOGRAPHY

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1 INTRODUCTION

A number of recent regulatory issues in the United States have created renewed interest in the development of more efficient methods for the analysis of radium isotopes in water samples. Radium has the lowest maximum permissible concentration in drinking waters among regulated radionuclides¹. A new rule by the US Environmental Protection Agency (EPA)² has created a new set of sampling requirements designed to better monitor the US water supply. Because of these changes, the more than 50,000 individual drinking water supplies in the US will need to perform incremental analyses for radium isotopes over the next couple years. This will create a large increase in the demand for radioanalytical services. A comparison of eight different methods for radium analysis was recently completed by Kohler, et al³. These available methods are lengthy, inconsistent, and time consuming. It is unlikely that the laboratory community will have sufficient capacity to provide the analyses required by the new US regulations, unless more efficient methods are available.

Additionally, in recent years, it has been discovered that a number of drinking water supplies in the eastern part of the US contain high levels of short-lived Ra-224. The currently approved methods for alpha emitting radium isotopes are all based on radon emanation. Due to the long ingrowth periods required by these methods, any Ra-224 in the sample decays away and goes undetected. A faster method for direct measurement of alpha emitting radium isotopes would allow for the detection and measurement of Ra-224.

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For these reasons, we have proposed the following alpha spectrometric method for determination of Ra-223, Ra-224 and Ra-226. It can be readily coupled with a rapid method for determination of Ra-228 to provide an efficient means of measurement of alpha and beta emitting isotopes of radium. This combined method is currently under review for approval by ASTM, International technical committee D19.04, *Radioactivity in Water*. The ultimate goal of this committee is approval of the method by US EPA for use in drinking water analyses.

2 EXPERIMENTAL

2.1 Standards

National Institute of Standards and Technology (NIST) traceable radionuclides ^{133}Ba and ^{226}Ra were used to characterize the radionuclides of interest.

2.2 Reagents and Materials

All reagents utilized in the analysis were American Chemical Society reagent grade; 0.1M HNO_3 ; 8M HNO_3 ; 0.095M HNO_3 ; concentrated HNO_3 ; 40% Na_2SO_4 ; 70% Na_2SO_4 ; concentrated H_2SO_4 ; 75 $\mu\text{g/ml}$ BaCl_2 ; and 1:1 acetic acid. Prepacked Ln Resin columns and cation exchange resin, 8% cross-linked, 100-200 mesh, hydrogen form were obtained from Eichrom Technologies, Inc. (Darien, IL, USA). Ln Resin is an extraction chromatographic resin which has di-(2-ethylhexyl) orthophosphoric acid as an extractant⁴. The resin has strong affinity for tri-valent species such as actinium and also separates several 'rare-earths'

2.3 Sample Preparation and Separation Procedure using Cation Exchange Resin and Ln Resin

A 500 to 1000mL aliquot of the sample is acidified with nitric acid to pH 2. Ten mL cation exchange resin is slurried in DI water and packed into 1.5 cm diameter columns. The column is preconditioned with 50 ml of 0.1M HNO_3 . After the acidified sample has passed through the cation exchange column, it is rinsed with 30 ml of 0.1M HNO_3 . Ra and Ba are eluted with 100 mL of 8M HNO_3 .

The eluted Ra/Ba fraction is then evaporated to dryness. The sample residue is re-dissolved in 10 mL of 0.095M HNO_3 . A pre-packed 2mL Ln Resin column is preconditioned with 5mL 0.095M HNO_3 . A cleaned, labeled beaker is placed under the column and the sample solution is loaded on the column. Three 5 ml rinse of 0.095M HNO_3 are passed through the column and collected. Radium passes through this column while actinides and rare earth elements are retained. This ensures decontamination of the radium fraction from many alpha emitters that could interfere in the alpha spectrum. The

combined load and rinse solution (containing radium) is evaporated to an approximate volume of 10 mL. The solution is then transferred to a 50 mL of centrifuge tube.

Although this paper will discuss only Ra-226 and Ra-224 measurements one can also measure Ra-228 via Ac-228 with this technique. Burnett, et al.⁵ demonstrated the use of Ln Resin for Ra-228 measurement of water samples. After the elution of the Ra/Ba fraction from the Ln column, Ac-228 can be eluted with 10 mL of 0.35M HNO₃.

A micro-precipitation of barium is carried out on the evaporated Ra/Ba fraction. This technique is a modified version of the one described in Sill 1987⁶. Seventy-five μ g of barium carrier is added to the centrifuge tube, followed by 3 mL of 40% Na₂SO₄ and a few drops of 1:1 acetic acid solution. The sample is gently stirred and then 0.2mL of a seeding suspension is added and mixed immediately. The sample is placed in a cold-water bath for at least 30 minutes. The solution is then filtered through a 0.1 micron, 25 mm diameter polypropylene filter. The filter is mounted on a planchet and counted for Ra-223, Ra-226 and Ra-224 by alpha spectrometry. A typical alpha spectrum for a sample containing Ra-224, Ra-226 and daughters is shown in figure 1. After the completion of alpha spectrometry counting the filter is then counted for Ba-133 by gamma spectrometry.

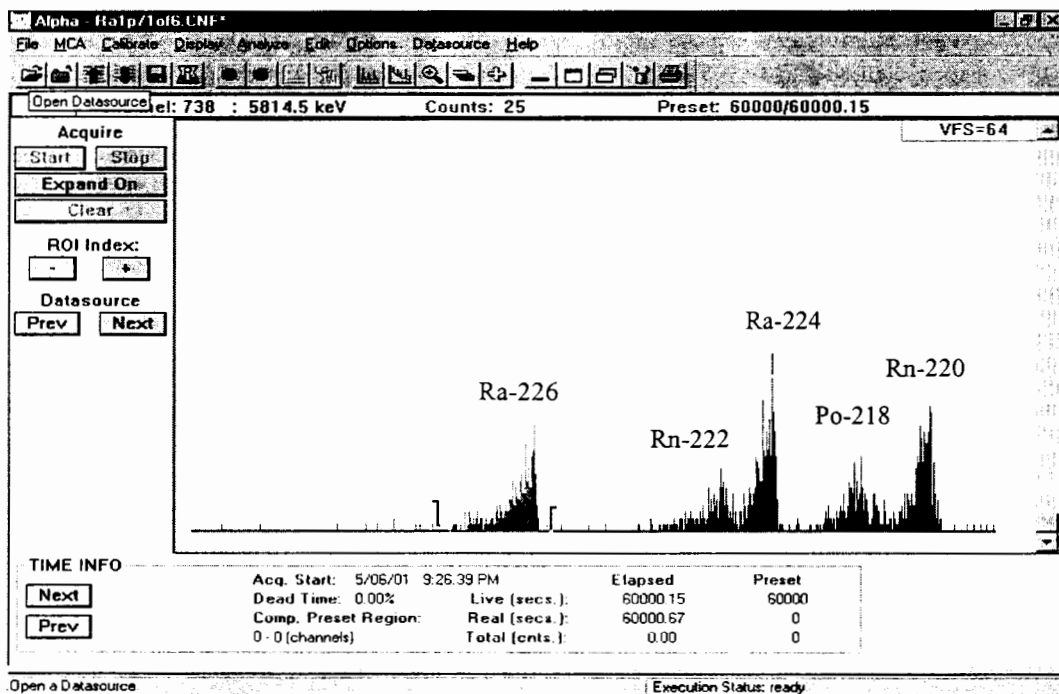


Figure 1. Alpha Spectrum of sample containing Ra-226, Ra-224 and daughters

3 RESULTS AND DISCUSSION

3.1 Water Samples

Table 1 summarizes the recoveries of Ra-226 tracers achieved by the method on DI and tap water samples. The Ra-226 recoveries averaged 85% on 0.5L DI water samples, 84% for 0.5 liter tap water and 93% on 1 liter tap waters.

Table 1. *Ra-226 recoveries in water samples*

Water Type	Volume	Ra-226 Yield (%)	Number of samples
DI water	0.5 L	85 ± 8	14
Tap water	0.5 L	84 ± 13	4
Tap water	1.0 L	93 ± 8	5

Several samples that had been previously tested by other laboratories with different techniques for Ra-226 were analyzed to validate the accuracy of this method. These included EPA cross check samples (September 18, 1998)⁷, and samples supplied by the New Jersey State Department of Health and Georgia Institute of technology. The results, reported in Table 2, compared to the known values well with no consistent bias high or low. The expected value shown for the EPA cross check sample is the reference value reported by EPA for the samples. The expected values for the samples supplied by

Water Type	Ba-133 Yields (%)	Eichrom Value pCi/L (mBq/L)	Exp. Value PCi/L (mBq/L)
EPA Cross check	95.7 ± 6	1.41 ± 0.17 (52.2 ± 6.3)	1.7 ± 0.5 (62.9 ± 18)
New Jersey	91	8.64 ± 1 (320 ± 37)	9.1 ± 0.5 (337 ± 18)
Georgia Tech WS14776	88	4.14 ± 0.58 (153 ± 21)	3.3 ± 0.3 (122 ± 11)
Georgia Tech S8933	88	22.6 ± 3 (836 ± 111)	18.0 ± 2 (666 ± 74)

the New Jersey State Lab and Georgia Tech were determined by their in-house laboratories using gamma spectrometry.

Table 2. *Ra-226 recoveries in cross check samples*

3.2 Matrix Effects

The first step in this procedure is a concentration of Ra and Ba on cation exchange resin, which does not have a high degree of selectivity for these elements over calcium and magnesium. Since Ca and Mg are often present in high concentrations in environmental waters, there is a potential for interference with the uptake of radium and barium by the cation exchange resin. Therefore, the effect of increasing amounts of these two elements on the uptake of radium and barium in this procedure was tested. Results, shown in Figure 2, indicated that, increasing concentrations of Mg did not have a significant impact on Ra recoveries even at levels as high as 1000ppm in a 500 mL sample. Calcium on the other hand, had a significant effect. Up to 200 ppm Ca, chemical recoveries of Ra were acceptable. Two samples with Ca content of 600 and 1000 ppm were analyzed. With these two samples, there was too much precipitate in the final alpha source preparation that they could not be counted.

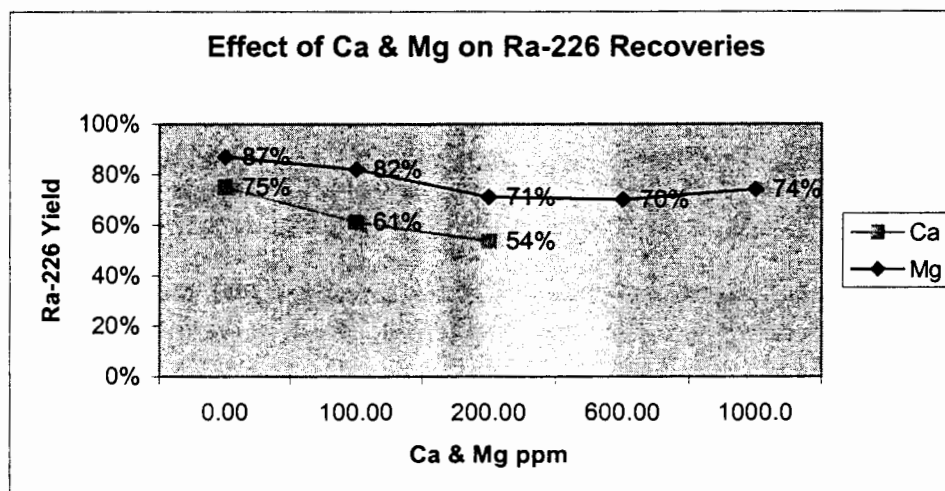


Figure 2. *Effect of Ca and Mg on Ra-226 Recoveries in 500 ml of sample*

In order to deal with samples with Ca levels higher than 200 ppm, we experimented with reducing the volume of the sample to 100 mL. Results of the experiment are shown in Figure 3. Ra-226 and Ba-133 spikes showed equal and acceptable chemical recoveries even up to 500 ppm Ca in a sample. These results show that reduction in sample volume can successfully address the calcium matrix issue. The comparable radium and barium

recoveries also indicate that the Ba-133 is a suitable yield monitor for radium in this method.

Most drinking waters contain no more than 200 ppm Ca so the analysis of 500 mL samples is acceptable. In those situations where the calcium content is greater than 200 ppm, a 100 mL aliquot can be analyzed. This will require longer counting times to achieve a given detection limit.

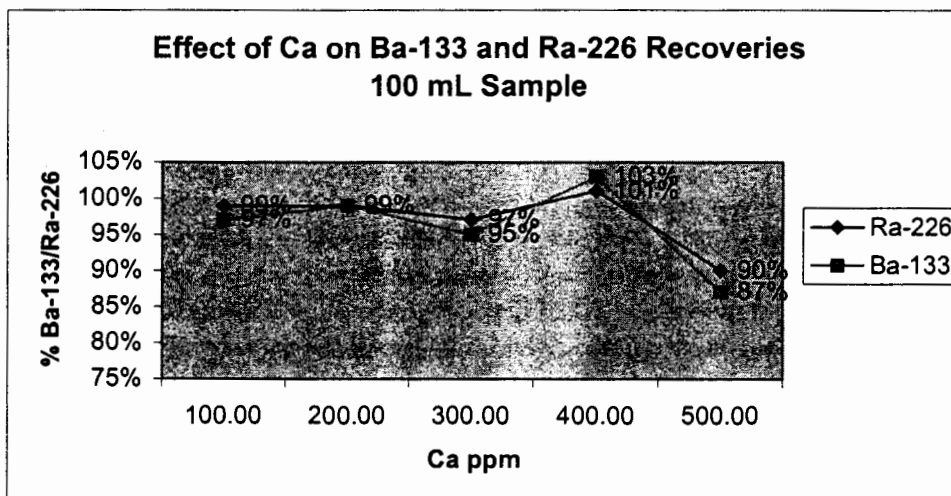


Figure 3. Effect on Ca on Ba-133 and Ra-226 recoveries in 100 mL sample

Table 3 summarizes the calculated detection limits achievable for various sample sizes and counting times, assuming 90% chemical yield. The current US EPA regulations require a detection limit of 1 pCi/L (37 mBq/L). This is readily achievable with 100-minute count time and 500 mL sample or 480-minute count time and 100 mL sample.

Table 3. Detection limits based on different volume and count time

Sample Volume	Count Time (minutes)	Detection Limits pCi/L
0.5 Liter	1000	0.09 (3.33 mBq/L)
0.5 Liter	240	0.3 (11.1 mBq/L)

0.5 Liter	100	0.8 (29.6 mBq/L)
0.1 Liter	480	0.9 (33.3 mBq/L)

4 CONCLUSION

The method described here shows promise as a more rapid alternative to existing methods for Ra-224 and Ra-226 measurements. Detection limits required by US EPA are achievable with reasonable sample sizes and short counting times. The applicability of this method to the European regulatory environment has not been determined. More demanding detection limits may require method improvements to accommodate larger sample sizes.

The most significant limitation to adoption of this method is regulatory approvals. It is our hope that the efforts of ASTM D19.04 should remedy this.

References

1. Code of Federal Regulations, Title 10, part 20, revised April 30, 1975
2. U.S. Environmental Protection Agency, "National Interim Primary Drinking Water Regulations", EPA-570/9-76-003 Washington, D.C.
3. M. Kohler, W.Presusse, B. Gleisberg, I. Schafer, T.Heinrich, and B.Knobus, *Applied Radiation and Isotopes*, 2002, 56, 387-392
4. E.P. Horwitz and C.A.A. Bloomquist, *J. Inorg. Nucl. Chem*, 1975 vol.17 425-434
5. W. Burnett and P.Cable, *Radioactivity & Radiochemistry*, 1995, Vol. 6, No. 3, 36-44
6. C.W. Sill, *Nucl. Chem. Waste Manage.* 1987, 7, 239-256
7. Uranium-Radium in Water Performance Evaluation Study, A Statistical Evaluation of the Sept 18, 1998 Data, Environmental Protection Agency, National Exposure Research Laboratory, Environmental Sciences Division, Las Vegas, Nevada"

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