

## RP450<sup>(a)</sup>

### Determination of Radium-226 in Aqueous Samples

The decision to use this method or a modified version of this method should be made during project planning (see Chapter 1). Project personnel, together with stakeholders, should determine the activities that need to be performed to ensure that this method is appropriate for use in the project (see Appendix B).

#### 1.0 Scope and Application

This method describes the separation of  $^{226}\text{Ra}$  in aqueous samples (groundwater, tap water, drinking water, biological samples, and dissolved soils) through ion exchange, electrodeposition, and analysis by alpha spectrometry. If  $^{224}\text{Ra}$  is present in the sample, low levels of this isotope can also be measured. This method has been tested by a single laboratory through application to low-level samples from drinking-water sources in the Chicago vicinity.

#### 2.0 Summary

A cation-exchange column is used to separate the analyte from other constituents in the sample (1 to 50 mL). After preconcentration and separation, the Ra is electrodeposited onto a stainless steel disc from a solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and HCl in the presence of microgram amounts of Pt. This electrodeposition method is direct, highly sensitive, and highly specific. After electrodeposition, the disc containing the analyte is placed in an alpha counter. Radium-224 is used as an internal tracer through standard additions.

Detection limits of the method, taken as three times the standard deviation of several reagent blank analyses, were  $(1.8 \pm 0.3) \times 10^{-4}$  Bq and  $(2.9 \pm 0.3) \times 10^{-4}$  Bq for  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ , respectively. Recoveries of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  ranged from 90% to 100%, and precision was calculated to be less than 5% for the determination of  $^{226}\text{Ra}$ .

#### 3.0 Interferences

The performance studies indicated that the presence of Ba in the water sample might result in a low yield during electrodeposition. However, most of the Ba is removed with the 1.5 M HCl column wash.

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(a) This method was supplied by J. S. Alvarado, K. A. Orlandini, and M. D. Erickson (Argonne National Laboratory, Argonne, Illinois).

The major interferences in the determination of the Ra isotopes by alpha spectrometry are  $^{234}\text{U}$  and  $^{230}\text{Th}$ . These two isotopes have major alpha-emission energies at 4.773 MeV and 4.684 MeV, respectively. These energies cannot be resolved from the spectral peaks of  $^{226}\text{Ra}$  (doubled at 4.602 and 4.784 MeV). Pretreatment of the sample is needed to remove U and Th before electrodeposition.

#### 4.0 Safety

No special safety precautions are indicated for this method.

#### 5.0 Apparatus and Materials

- Ion-exchange column (10-cm length, 0.5-cm ID)
- Highly polished stainless steel disc (for use in alpha spectrometry)
- Electrodeposition cells for stainless steel plating {Orlandini et al. (1991) describe one example of an electrodeposition apparatus.}
- Alpha spectrometer with standard surface barrier detector

#### 6.0 Reagents

Reagent-grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to American Society for Testing and Materials (ASTM) specification D 1193, Type II (or better), unless otherwise indicated.

- 1.5 M HCl
- 6.0 M HCl
- Radium-224 standard solution (A steady supply of  $^{224}\text{Ra}$  may be obtained from an old stock of  $^{232}\text{U}$ . The  $^{224}\text{Ra}$  is calibrated against a  $^{236}\text{U}$  standard from the National Institute of Standards and Technology.) Alternatively,  $^{225}\text{Ra}$  or  $^{223}\text{Ra}$  may be used as a tracer. The  $^{224}\text{Ra}$  isotope was preferred because, as a naturally-occurring isotope, its use would minimize the creation of mixed waste.

- Cation exchange resin (AG 50W-X8), 100 to 200 mesh in hydrogen form, or equivalent
- 0.12 M  $\text{H}_2\text{PtCl}_6$  in  $\text{HCl-HNO}_3$  (3:1)
- Electroplating solution containing 0.17 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 0.14 M  $\text{HCl}$

## 7.0 Sample Collection, Preservation, and Handling

Aqueous samples should be acidified to  $\text{pH} < 2$  with  $\text{HCl}$  or  $\text{HNO}_3$ . No other preservation or storage procedures are required.

## 8.0 Procedure

Figure 1 outlines the separation scheme for the determination of Ra.

- 8.1** To an aliquot of sample (1 to 50 mL), concentrated  $\text{HCl}$  or  $\text{HNO}_3$  is added until  $\text{pH} = 1$ .

*No effect has been observed on the sample uptake by the cation-exchange column when  $\text{HNO}_3$  or  $\text{HCl}$  is used to acidify the sample.*

- 8.2** A standard addition is used to monitor the quality of each analysis (assuming that the chemical yields from duplicate aliquots will be the same). Two aliquots of each sample are used. The first sample is spiked with  $^{224}\text{Ra}$ , and the second is analyzed without spike. If  $^{224}\text{Ra}$  is present in the sample, the signal produced in the counting process is subtracted from the signal produced by the sample containing the spike.

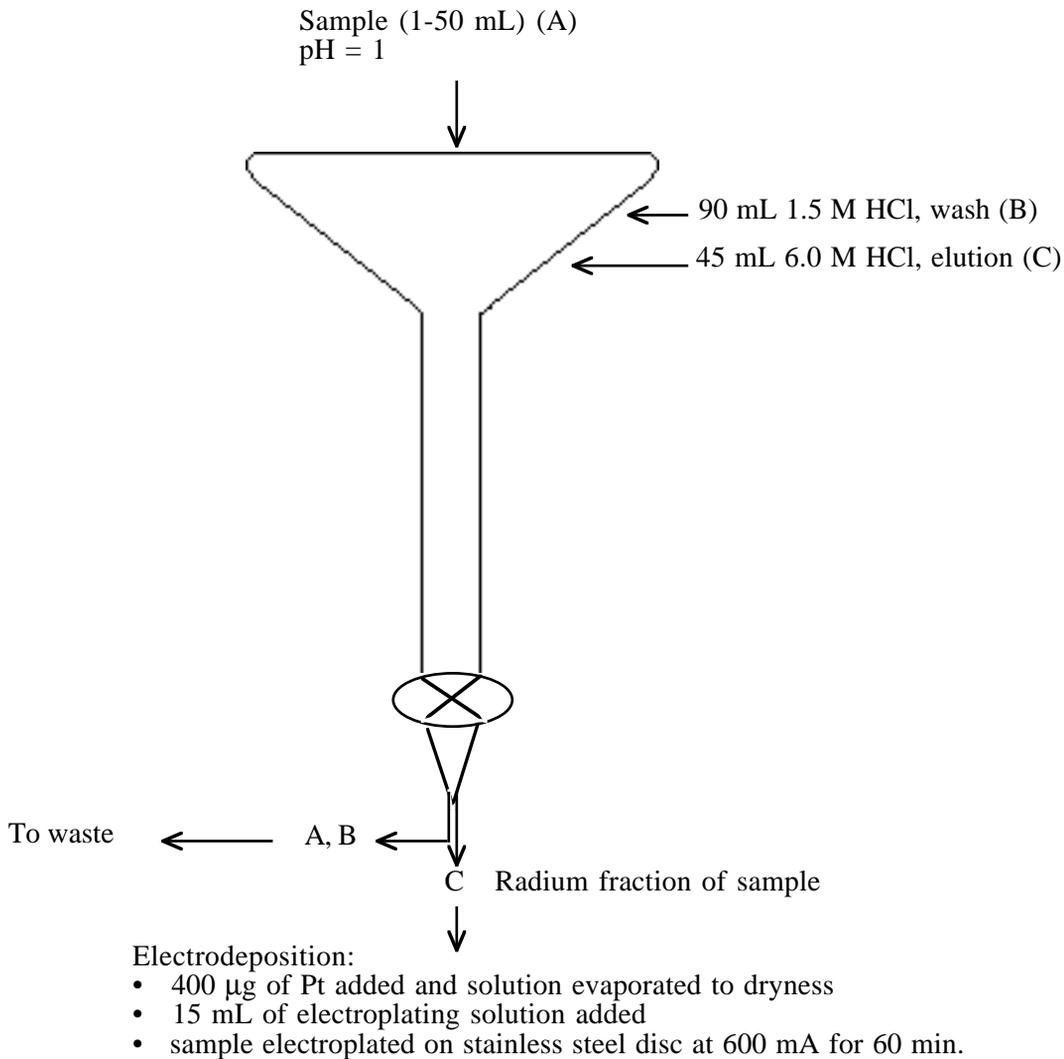
- 8.3** A column (10-cm length, 0.5-cm ID) is packed with 1 g of dry, analytical-grade AG 50W-X8 resin, 100 to 200 mesh in hydrogen form. The cation-exchange column is pretreated with 20 mL of 1 M  $\text{HCl}$ .

- 8.4** The sample is then loaded onto the column. When the sample has just loaded on the column, it is washed with 90 mL of 1.5 M  $\text{HCl}$ .

*Washing with 1.5 M  $\text{HCl}$  removes most of the  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Ba}$ ,  $\text{U}$ ,  $\text{Th}$ , and  $\text{Np}$ .*

- 8.5** The Ra is eluted from the column with 45 mL of 6 M  $\text{HCl}$ .

- 8.6** Ten microliters of 0.12 M  $\text{H}_2\text{PtCl}_6$  (~400  $\mu\text{g}$  Pt) solution are added to the sample solution.



**Figure 1.** Separation Scheme for the Determination of Radium

- 8.7** The Ra solution is evaporated to dryness, and the residue is dissolved in 15 mL of electroplating solution {0.17 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 0.14 M HCl}. The initial pH of this solution is 2.6.
- 8.8** The sample is then electrodeposited onto a highly polished stainless steel disk. The stainless steel is used as a cathode, and the platinum electrode near the surface is used as the anode. Each electrodeposition is carried out at 600 mA ( $0.2 \text{ A/cm}^2$ ) for 60 min.
- Coprecipitation may be used; however, optimal parameters have not been evaluated. Also, some peak broadening may occur with coprecipitation.*
- 8.9** After electrodeposition, the disc containing the analyte is counted by alpha spectrometry.

## 9.0 Calculations

Radium-224 is used as an internal tracer through standard additions. Averages of the alpha peaks produced by  $^{224}\text{Ra}$  (5.685 MeV, 94%) and its daughters  $^{220}\text{Rn}$  (6.287 MeV, 100%) and  $^{216}\text{Po}$  (6.78 MeV, 100%) are used to calculate the yield and concentration of each isotope in the standard and sample.

A correction factor is used for the decay of  $^{224}\text{Ra}$  from the time of separation from the  $^{232}\text{U}$ - $^{228}\text{Th}$ - $^{224}\text{Ra}$  equilibrium and during the counting period. The correction factor is calculated as follows:

$$\lambda = \frac{\ln 2}{t_{1/2}} \quad (1)$$

where

$$\begin{aligned} \lambda &= \text{decay constant} \\ t_{1/2} &= \text{half-life (3.66 days for } ^{224}\text{Ra)} \end{aligned}$$

$$D = \frac{e^{\lambda \Delta t} \cdot (\lambda \cdot \text{RT})}{1 - e^{-\lambda \text{RT}}} \quad (2)$$

where

$$\begin{aligned} D &= \text{decay factor for } ^{224}\text{Ra} \\ \Delta t &= \text{decay time between U separation (step 8.4) and beginning of sample count} \\ \text{RT} &= \text{elapsed real time for the counting period.} \end{aligned}$$

The activity of the  $^{224}\text{Ra}$  tracer in the sample is calculated by using the net counts, corrected by the counts present in the sample, according to the following equation:

$$A_{^{224}\text{Ra}} = \frac{(C_a - C_s) \cdot D}{\epsilon \cdot T \cdot V} \quad (3)$$

where

$A_{^{224}\text{Ra}}$	=	activity of $^{224}\text{Ra}$
$C_a$	=	net counts of $^{224}\text{Ra}$ in tracer at separation time (step 8.4)
$C_s$	=	net counts of $^{224}\text{Ra}$ in sample at separation time (step 8.4)
$\epsilon$	=	efficiency of counter
$T$	=	counting time
$V$	=	volume added.

The chemical yield (Y) is calculated at a constant time relative to the standard.

$$Y = \frac{A_{^{224}\text{Ra}}}{A_{\text{tracer}}} \quad (4)$$

where  $A_{\text{tracer}}$  = the  $^{224}\text{Ra}$  activity added to the sample.

Finally, the activity of  $^{226}\text{Ra}$  in the sample is calculated using the net counts (background-corrected), according to the following equation:

$$A_{^{224}\text{Ra}} = \frac{C_s}{\epsilon \cdot T \cdot k \cdot Q \cdot Y} \quad (5)$$

where

$C_s$	=	net counts of $^{226}\text{Ra}$ in sample
$k$	=	conversion factor for desired reporting units
$Q$	=	sample quantity (volume or mass).

## 10.0 Quality Control

The use of this method either as is or with modifications should be supported by appropriate quality control procedures (e.g., as outlined in Chapter 3). One blank per sample batch should be run to detect contamination. Two aliquots of each sample should be used. The first sample should be spiked with  $^{224}\text{Ra}$ , and the second sample should be analyzed without a spike to determine whether any  $^{224}\text{Ra}$  is in the sample.

## 11.0 Method Performance

The method performance was developed at a single laboratory and has been previously reported (Alvarado et al., 1995). An example of a Ra alpha spectrum is provided in Figure 2.

### 11.1 Linearity and Limits of Detection

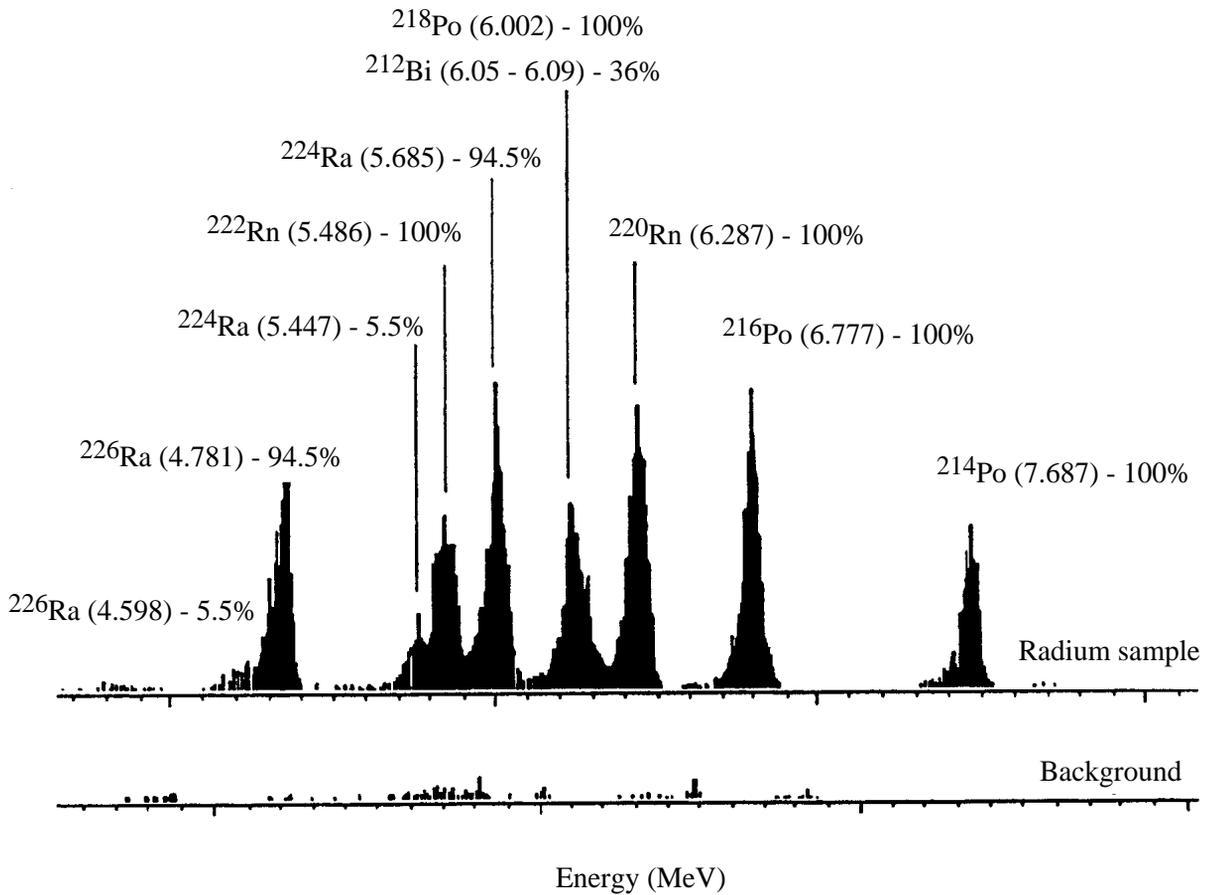
The system produced a linear response when solutions ranging from 0.0034 Bq/mL to 0.34 Bq/mL of  $^{226}\text{Ra}$  were used. The calibration plots had correlation coefficients ( $r^2$ ) of 0.9946.

Detection limits are defined as the smallest concentration of radioactive material in a sample that will yield a net count above the system background and will be detected with 95% probability, with only 5% probability of falsely concluding that the blank observation represents a real signal. The instrument background levels were routinely measured at 0.5 counts per 1000 min. The limits of detection for a 1000-min counting period, calculated for background only, were  $(2.6 \pm 0.3) \times 10^{-5}$  Bq for both  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$ . The observed detection limits of the procedure, taken as three times the standard deviation of several reagent blank analyses, were  $(1.8 \pm 0.3) \times 10^{-4}$  Bq for  $^{226}\text{Ra}$  and  $(2.9 \pm 0.3) \times 10^{-4}$  Bq for  $^{224}\text{Ra}$ .

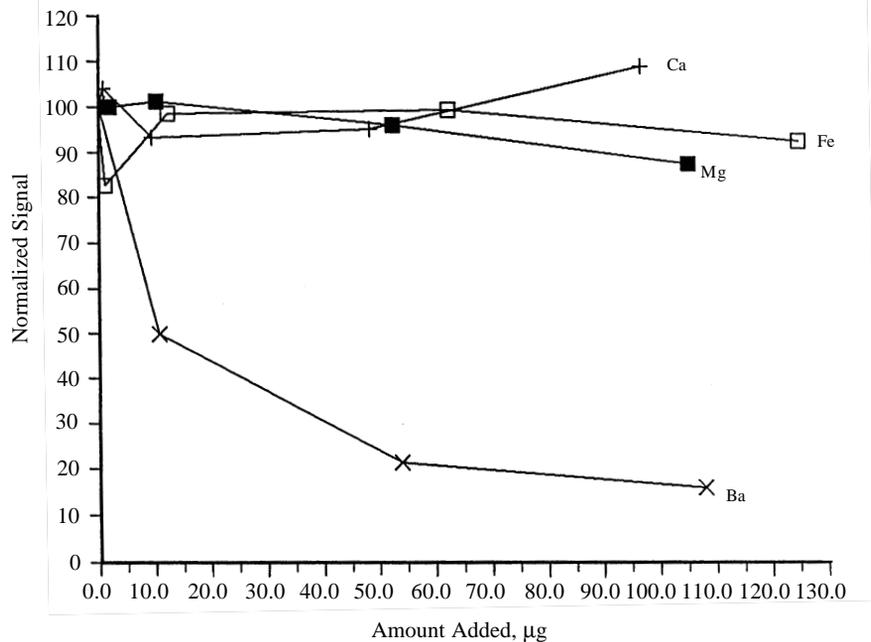
### 11.2 Matrix Effects

Nitrates of Ca, Mg, Ba, and Fe were used to study their potential effects on the separation and electrodeposition of  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$ . Relatively low concentrations (up to 100  $\mu\text{g}$ ) of Ca, Fe, and Mg caused a slight decrease in the Ra signal. However, the Ra signal was markedly depressed when Ba was added. The signal was reduced to 50% of the original signal when 10  $\mu\text{g}$  of Ba were added. The washing step used during preconcentration and extraction was sufficient to eliminate interferences like Fe, Mg, Ca, Ba, U, Th, and Np. These results are summarized in Figure 3.

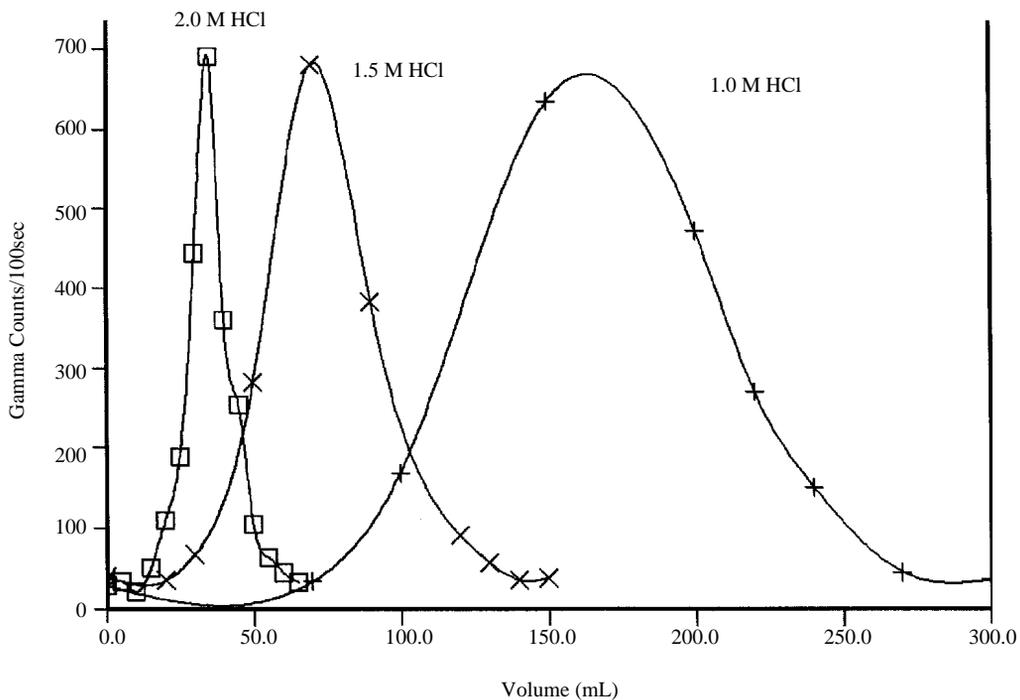
Barium as  $^{133}\text{Ba}$  was followed to observe the elution behavior of the system. Figure 4 shows the elution peaks for the barium at different acid molarities. By using



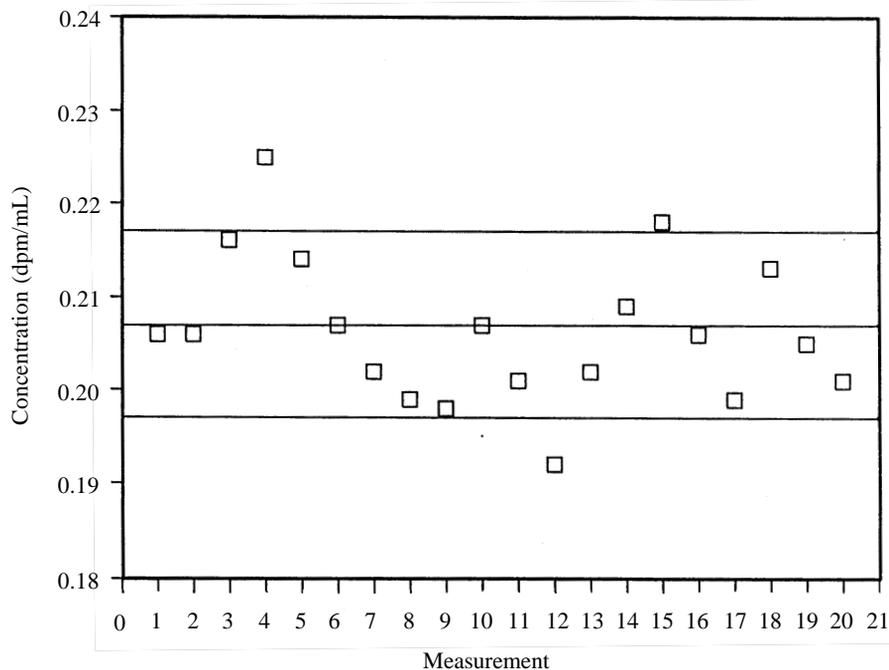
**Figure 2.** Radium Alpha Spectrum



**Figure 3.** Matrix Effects on <sup>224</sup>Ra Electrodeposition with Ca, Mg, Fe, and Ba



**Figure 4.** Experimental Elution Curves for Barium-133



**Figure 5.** Precision of the Radium-226 Analysis

approximately 100-mL wash volume of 1.5 M HCl, barium was eliminated, and Ra recoveries higher than 92% were obtained. Samples of  $^{234}\text{U}$  and  $^{230}\text{Th}$  (no  $^{226}\text{Ra}$ ) were also run, and these isotopes were also eliminated (Alvarado et al. 1995).

### 11.3 Accuracy and Precision

Precision measurements are illustrated in Figure 5. The data represent quadruplicate measurements on five consecutive days at a  $^{226}\text{Ra}$  concentration of  $3.45 \times 10^{-3}$  Bq/mL in water. For 20 spike analyses, the average value obtained was  $3.42 \times 10^{-3}$  Bq/mL, with a relative standard deviation (RSD) of 4.6%. The error for this set of experiments was 1.1%. In a separate experiment, the recovery of  $^{224}\text{Ra}$  was 98% with an RSD of 0.6%. For  $^{226}\text{Ra}$ , the recovery was 93% with an RSD of 4.9%.

Table 1 compares Ra measurements in this work with the results obtained for  $^{226}\text{Ra}$  by the gas-emanation technique (Method RA-03, HASL 300) (Chieco et al. 1990) and other reported values. Well water from Kimbell, Kansas, drinking water from the Illinois area, and dissolved bones were studied.

## 12.0 References

Alvarado, J. S., K. A. Orlandini, and M. D. Erickson. 1995. "Rapid Determination of Radium Isotopes by Alpha Spectrometry." *J. Radioanal. Nucl. Chem.* , 194, pp. 133-138.

Chieco, N. A., D. C. Bogen, and E. O. Knutson, Eds. 1990. "Method RA-03." *Environmental Measurements Laboratory Procedures Manual*, 27th Ed., HASL-300 , U.S. Department of Energy, Environmental Measurement Laboratory, New York.

Orlandini, K. A., J. S. Gaffney, and N. A. Marley. 1991. "An Improved Technique for the Rapid Assay of Radium Isotopes in Water." *Radiochim. Acta* 55, p. 205.

## 13.0 Further Reading

Hamilton, T. F., V. M. McRae, and J. D. Smith. 1994. "Radium Isotope Determination by Alpha-Spectrometry After Electrodeposition from Solution with Added Platinum." *J. Radioanal. Nucl. Chem.* 177, p. 365.

Roman, D. 1984. "Electrodeposition of Radium on Stainless Steel from Aqueous Solutions." *Int. J. Appl. Radiat. Isot.* 35, p. 990.

**Table 1.** Results of Radium Determinations in Aqueous Samples

	<sup>226</sup> Ra (Bq/L)	
	<u>Measured (This Method)</u>	<u>Reported (Other Methods)</u>
<b>Well Water</b>		
Kimbell #1	20.3 ± 0.7	21.8 ± 1.0 <sup>(a)</sup>
<b>Drinking Water</b>		
IL-0773-1	0.038 ± 0.004	0.039 ± 0.002 <sup>(b)</sup>
IL-0774-1	0.033 ± 0.004	0.033 ± 0.002 <sup>(b)</sup>
IL-0775-1	0.028 ± 0.003	0.028 ± 0.002 <sup>(b)</sup>
IL-0776-1	0.026 ± 0.003	0.025 ± 0.001 <sup>(b)</sup>
<b>Dissolved Bones</b>		
DB-116-470A	3.1 ± 0.2 <sup>(c)</sup>	2.88 ± 0.06 <sup>(b,c)</sup>
DB-116-230A	5.8 ± 0.3 <sup>(c)</sup>	7.1 ± 0.2 <sup>(b,c)</sup>
<b>Other</b>		
STD sample	0.36 ± 0.03	0.37 ± 0.06 <sup>(d)</sup>

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- (a) From Orlandini et al. 1991.  
(b) Measured by gas-emanation technique.  
(c) Value reported in Bq.  
(d) Round-robin reported value.