BW295

DETERMINATION OF RADIUM-228 IN NATURAL WATERS USING EXTRACTION CHROMATOGRAPHIC RESINS

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Accepted for Publication In: *Radioactivity and Radiochemistry*
Volume 6, No. 3
September 30, 1995

ABSTRACT

We have developed a procedure for determination of ^{228}Ra ($t_{1/2}$ = 5.75 y) in natural waters using either the extraction chromatographic resins TRU·Spec™ or Ln·Spec™ to isolate the direct daughter, ^{228}Ac, just before low-level counting. These separations are shown to be quantitative, simple, relatively fast, and free from most interferences. The recommended procedure effectively eliminates the need to perform the multiple precipitations and solvent extractions required by conventional techniques.

The method uses a standard $BaSO_4$ co-precipitation with ^{133}Ba as an internal tracer to preconcentrate radium isotopes from a 1-2 liter water sample. This is followed by a metathesizing process using K_2CO_3 to convert the $BaSO_4$ to the more soluble $BaCO_3$ form. After the ^{133}Ba yield determination, the sample (in HNO_3) is stored for ≥30 hours to allow ingrowth of equilibrium amounts of ^{228}Ac ($t_{1/2}$ = 6.14 h) from the ^{228}Ra in the sample. This solution is then loaded onto a chromatographic column prerinsed with HNO_3 followed by a rinse with sufficient HNO_3 to completely flush out barium, radium, lead, and other common elements which may be contained in the sample load. Actinium is then eluted with either HCl or more concentrated HNO_3 and is ready for low-level beta-particle counting after mounting by filtration or evaporation. We estimate a detection limit of ≤1.0 pCi/L in approximately 30 minutes of counting using a proportional counter with a 1.0 cpm total beta background, a ^{133}Ba yield of 80%, and a 2-liter sample volume.

INTRODUCTION

Marine, earth, and environmental scientists often have a need to determine radium isotopes in natural waters. The naturally-occurring isotopes of radium, especially the longer-lived ^{226}Ra ($t_{1/2}$ = 1620 y) and ^{228}Ra ($t_{1/2}$ = 5.28 y), are of health concern as radium is known to be a "bone seeking" element. Other isotopes of radium, such as ^{224}Ra ($t_{1/2}$ = 3.6 d) and ^{223}Ra ($t_{1/2}$ = 11.4 d) have been used a tracers of various processes in the marine and terrestrial environments (Moore, 1976; Li et al., 1979; Rama *et al.*, 1987; Cochran, 1992; Burnett and Tai, 1992). While direct counting techniques exist for the alpha-particle-emitting radium isotopes ^{223}Ra, ^{224}Ra, and ^{226}Ra (Sill, 1987a), virtually all the techniques for ^{228}Ra are based either on analysis of its direct beta-particle-emitting daughter, ^{228}Ac, or its alpha-particle-emitting granddaughter, ^{228}Th. A survey of the technical literature from 1967-1980 by Noyce (1981) reported 17 methods for determining ^{228}Ra in water. Most of these methods relied on ^{228}Ac separation although a few used ^{228}Th or ^{224}Ra counting. The ^{228}Th approach, while very sensitive because of the very low background characteristic of alpha spectrometry, requires an ingrowth period of at least several months.

Most methods used today for analysis of ^{228}Ra separate ^{228}Ac by liquid-liquid extraction into bis(2-ethylhexyl) phosphoric acid, or HDEHP (U.S. EPA, 1984). We set out to investigate the use of extraction chromatographic resins for separation of Ac without the waste that normal liquid-liquid extractions produce and to devise a simple scheme that would be amenable to producing results for both ^{228}Ra, ^{226}Ra, and perhaps other radium isotopes in the same sample preparation. To this end, we evaluated two types of extraction chromatographic resins supplied by Eichrom Industries, Inc. (8205 South Cass Avenue, Suite 107, Darien, Illinois 60561): (i) TRU·Spec™ — a polymeric support, Amberlite XAD-7 beads, impregnated with the extractant 0.75M CMPO, octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide in TBP, tri-n-butyl phosphate; and (ii) Ln·Spec™ — HDEHP impregnated upon Amberlite XAD-7 80-160 μm beads. The preparation and principle of use of these resins has been described in several previous publications (Dietz and Horwitz, 1993 and references therein) and will not be repeated here. In addition to showing that both of these resins may be successfully used to isolate Ac, we also show how they perform with respect to the major interfering nuclides that one might encounter when analyzing ^{228}Ra both in natural waters and in those contaminated with artificial radionuclides.

EXPERIMENTAL

A series of gamma-ray-emitting tracers were used to evaluate the elution characteristics of the extraction chromatographic resins. These tracers included ^{228}Ra-^{228}Ac and ^{133}Ba (EPA Environmental Monitoring Systems Laboratory, P.O. Box 93478, Las Vegas, NV 89193-3478); ^{226}Ra-^{214}Pb-^{214}Bi (NIST, Gaithersburg, Maryland 20899-0001); ^{210}Pb, ^{207}Bi, and ^{88}Y (Isotope Products, 1800 N. Keystone Street, Burbank, California 91504, CA); and ^{234}Th which we prepared by milking a uranyl nitrate solution following the method of Goldberg and Koide (1972). Elution curves were generated by combining whatever tracers were used for a particular run into one load solution which was added 1 mL at a time to a prepacked column of TRU·Spec™ resin or the same amount (0.7 g) of Ln·Spec™ resin which we packed into the same type of small plastic columns (approximately 6 x 0.9 cm, manufactured by Isolab Inc., Akron, OH). All elutions from the extraction chromatographic columns were collected sequentially in 1-mL increments in plastic vials which were then directly counted in a 120cc well-type intrinsic germanium detector interfaced to a Canberra Industries Series 90 MCA. Final ^{228}Ac sample mounts, prepared by CeF_3 co-precipitation and filtration using Gelman 25-mm Metricel™ filters, were counted in a Canberra Model 2404 gas flow proportional counter.

The reagents required for the TRU·Spec™ procedure included: a barium chloride carrier (30.0 mg/mL) which was prepared by dissolving 13.3 grams reagent grade $BaCl_2$ in 250-mL double deionized water (DDW); a potassium carbonate solution (50% w/w);

concentrated H_2SO_4; 2M HNO_3 prepared by diluting 12.5-mL concentrated 15.8M HNO_3 to 100 mL with DDW; and 1M HCl (prepared by diluting 8.3-mL concentrated 12M HCl to 100 mL with DDW). The reagents used for the Ln·Spec™ procedure were basically the same as the TRU·Spec™ method except for 0.095M HNO_3 (prepared by diluting 3.0-mL concentrated 15.8M HNO_3 to 500 mL with DDW) and 0.35M HNO_3 (prepared by diluting 11.0 mL concentrated 15.8M HNO_3 to 500 mL with DDW).

RESULTS AND DISCUSSION

General Considerations and Preconcentration of Radium

Because of the nature of the analysis there were two principal requirements for the chemical separation: (i) the separation and subsequent mounting of Ac must be quantitative; and (ii) the final Ac fraction must be as free as possible from interfering nuclides. The separation and mounting procedures must be quantitative because the ^{133}Ba yield determination will only correct for losses up to the point in the procedure that the sample is loaded onto the column for separation of Ac. At that point ^{228}Ac is in secular equilibrium with ^{228}Ra which has been corrected for loss by the barium tracer. Potential radioactive interferences in this method would include any beta-particle-emitting radionuclide in one of the natural decay chains with a half-life of tens of minutes or longer. This would include ^{227}Ac, and isotopes of thorium (^{234}Th, ^{231}Th), bismuth (^{214}Bi, ^{210}Bi), and lead (^{214}Pb, ^{212}Pb, ^{211}Pb, ^{210}Pb). Should contamination from artificial nuclides be possible, interferences from ^{90}Sr (^{90}Y) and radioactive rare earth elements (^{140}La, ^{147}Pm, etc.) must be considered as well.

We use a standard $BaSO_4$ co-precipitation, with ^{133}Ba as an internal tracer, to preconcentrate radium isotopes from a 0.5-2 liter filtered water sample. This is followed by a metathesizing process using K_2CO_3 to convert the $BaSO_4$ to the more soluble $BaCO_3$ form. Further points concerning the preconcentration and conversion process are summarized below and may be found in somewhat more detail in Burnett and Tai (1992). After the ^{133}Ba yield determination via gamma-ray counting with either a NaI or HPGe detector, the sample (in HNO_3) is stored for ≥30 hours to allow ingrowth of equilibrium amounts of ^{228}Ac ($t_{1/2}$ = 6.14 h) from the ^{228}Ra in the sample. At this point the sample is ready for loading onto a column for actinium separation.

TRU·Spec™ Separations

The elution curves for the TRU·Spec™ runs (**Fig. 1**) show that barium, lead, and radium pass directly through the resin as expected when loaded in 5 mL of 2M HNO_3 and rinsed with an addition 5 mL of the same solution. The actinium is retained on the column under these conditions and may be effectively eluted by addition of 5-10 mL of 1M HCl. Bismuth is quantitatively retained on the column through the actinium elution and, if desired, may be eluted with 6M HCl.

Although these experimental conditions are very suitable for most samples, our observations with hundreds of actual samples have suggested that a few problems remain in special circumstances. For example, water samples that contain high uranium and have been acidified will acquire significant ^{234}Th concentrations which will be eluted together with the Ac fraction following this procedure. We found that this problem can be resolved by eluting Ac with 10-15 mL of 3M HCl (instead of 1M HCl) which prevents Th and Bi breakthrough but still quantitatively elutes Ac. We have also encounted occasional interferences in samples containing high ^{90}Sr (^{90}Y) and ^{212}Pb. The yttrium interference was resolved by loading and rinsing the sample in 0.5M HNO_3 instead of 2M HNO_3. Apparently, the Y has a higher K_D under these conditions and doesn't breakthrough while Ac may be eluted as normal in 1-3M HCl (Burnett et al., 1993).

Unfortunately, samples with high ^{212}Pb relative to the amount of ^{228}Ac have continued to be a problem. The interference was recognized by the approximately 11-hour half-life determined by repetitive counting of selected samples (^{212}Pb $t_{1/2}$ = 10.64 h). There appears to be a small amount of Pb retention on TRU·Spec™ resin and, should the concentration be high enough, the small amount of crossover into the actinium field causes a significant interference. Since Pb is not strongly bound on TRU·Spec™ from dilute HNO_3, further rinsing would eliminate this problem. Unfortunately, only a limited amount of 0.5-2.0M HNO_3 can be used as a rinse before Ac begins to breakthrough. Our measurements have shown that Ac will begin to breakthrough just a little over 10 mL, depending upon the concentration of HNO_3. Thus, even though we were able to obtain excellent results on many samples using the TRU·Spec™ approach, there was a need to investigate a resin with better retention characteristics for Ac.

Ln·Spec™ Separations

This resin is designed for retention and separation of the lanthanide group of elements, the so-called "rare-earths". The HDEHP extractant thus has a strong affinity for tri-valent species such as actinium. We found that we could depend upon having excellent retention characteristics for Ac when the sample was loaded and rinsed in 0.095M HNO_3 and eluted with 0.35M HNO_3 (**Fig. 2**). We have determined experimentally that a 15 mL rinse with 0.095M HNO_3 does not cause any Ac breakthrough and is sufficient to ensure that so there is no residual Pb. Bismuth, yttrium, and thorium are all retained by the resin during the elution of Ac. If desired, bismuth may be eluted with 2.0M HNO_3-0.1M oxalic acid, and yttrium may be effectively eluted with 3.0M HCl. Although we did not investigate elution schemes for thorium, we did confirm that it does not interfere with any of the elutions shown in Figure 2. Thus, this procedure appears to offer quantitative separation of Ac from most elements which have potentially interfering beta-particle-emitting radionuclides, i.e., Pb, Bi, Th, and Y. Interferences from other radioactive rare earth elements is also possible although not all of them should be extracted under these conditions (Horwitz and Bloomquist, 1975; Horwitz et al., 1976). In addition, other distinctions from ^{228}Ac can be made based on energy and/or half-life. For example, the other naturally-occurring beta-particle-emitting isotope of actinium, ^{227}Ac, can be distinguished by its soft beta (0.045 MeV relative to the 1.2 and 2.1 MeV betas of ^{228}Ac) and its much longer half-life (21.8 y).

Recommended Procedure

Radium Pre-Concentration, Conversion, and Yield Determination:

We usually start with a 0.5-2 liter acidified, filtered water sample although one could decant from an unfiltered sample if care was taken to exclude particulates (**Fig. 3**). After addition of 1 mL barium carrier (~30 mg Ba) and 1 mL ^{133}Ba tracer (~4000 dpm), 10 mL of concentrated H_2SO_4 is added to precipitate $BaSO_4$. We find that heating with occasional stirring for about two hours helps to cure the precipitate and improves the settling characteristics. After settling (usually overnight for convenience), the bulk of the supernatant liquid is decanted or aspirated and the remainder transferred to a centrifuge tube for final separation. The precipitate is washed 2-3 times with DDW to remove excess H_2SO_4. The pH may be monitored with test strips to evaluate when the excess acidity has been removed. We normally stop rinsing when the pH reaches about 6.

In order to convert the $BaSO_4$ to the more soluble $BaCO_3$ form, we metathesize by adding 1 mL of the K_2CO_3 solution, an additional 2-3 mL DDW, and by heating the centrifuge tube over a low flame until boiling. This is usually done with constant stirring using a glass stirring rod. This procedure continues for a few minutes until the volume is reduced to about 1 mL and then the resulting slurry is cooled. The process is repeated 2-3 times after addition of 3-5 mL DDW before each cycle. Another option, which is particularly suitable for batch work, is to do the conversion process in a microwave oven. We have done this with the same Pyrex centrifuge tubes that we use for the flame conversion in a standard microwave in just a few minutes. The specific conditions will depend on the power of the oven used, number of samples being converted, and other variables.

The resulting precipitate, now in the form of $BaCO_3$, is washed with 2-3 portions of 15-20 mL DDW to remove excess CO_3^{2-} and SO_4^{2-} ions. This is important because the presence of sulfate could cause reprecipitation of barium during the dissolution of barium carbonate with HNO_3. We generally wash until the pH, initially about 12, is reduced to approximately 7. These solids should now dissolve, with gentle heating if necessary, in 5 mL of the Ln·Spec™ load solution, 0.095M HNO_3. If any solids remain, the supernatant can be separated by centrifugation and the remaining solids can be reacted again with the K_2CO_3 solution. Alternatively, if the ^{133}Ba recovery is acceptable (≥80%), the residual solids can be discarded. We measure the barium yield against a reference sample (same amount of ^{133}Ba dispensed into a counting vial and adjusted to the same geometry as the samples) in a well-type NaI detector. We have not observed any differences which may exist between the chemical recoveries of radium and barium although we recognize that small discrepancies are possible because of slight variations in their chemistries (Sill, 1987a). At this point, we hold the sample for at least 30 hours to ensure sufficient time to achieve secular equilibrium between ^{228}Ra and ^{228}Ac.

Actinium Separation:

We pre-rinse the Ln·Spec™ column with 10 mL of 0.095M HNO_3, and load the sample after bringing the total volume to 10 mL by addition of 5 mL of 0.095M HNO_3 (this extra 5 mL can be used to rinse through the counting vial used for the ^{133}Ba yield measurement). After the sample has passed through the column, we rinse with three 5-mL portions of 0.095M HNO_3. The date and time at the beginning of this rinse cycle is noted as the approximate time of separation of ^{228}Ac from ^{228}Ra for subsequent decay corrections. After the final rinse is complete, a clean plastic disposable cup is positioned under the column and Ac is quantitatively eluted with 10 mL of 0.35M HNO_3. A source is prepared from this solution by addition of 50 μg of Ce as a carrier which is precipitated as CeF_3 by addition of 1.0 mL concentrated HF. After standing approximately 30 minutes to ensure complete precipitation, the CeF_3 is filtered onto 25-mm diameter, 0.1 μm Gelman polyethylene Metricel™ filters by the methods described in Sill (1987b). We have found that quantitative recovery of Ac is not a problem following this procedure if one exercises reasonable care. Another option for source preparation would be to simply evaporate the final elution volume (10 mL of 0.35M HNO_3) into a counting planchet. If one decided to employ this alternative approach, tests should be performed to assess absorption and efficiency parameters. We prefer the filtration approach because of its reproducible mass loading (constant absorption) and counting geometry.

If only ^{228}Ra is being analyzed, the sample load and rinse may either be discarded or saved for re-analysis after sufficient ingrowth time for the ^{228}Ac. In addition, since all radium isotopes (once corrected for the barium yield) should be in the combined sample and rinse fractions, this may be retained for analysis of ^{226}Ra by other standard techniques including: radon emanation (Key et al., 1979; Mathieu et al., 1988); PERALS spectrometry (Burnett and Tai, 1992); or alpha spectrometry (Sill, 1987a). PERALS spectrometry and alpha spectrometry can also provide information on ^{223}Ra and ^{224}Ra.

Counting and Activity Calculation

All samples are counted in a low-background, gas flow proportional counter. During the development work for this technique, we generally counted samples for several hours or overnight in order to follow the ^{228}Ac decay and to improve counting statistics. For routine work, we find that a minimum detectable activity (MDA) of <1.0 pCi/L may be obtained for a 2-liter sample with a 80% barium recovery in less than 30 minutes. Using similar assumptions, we calculate that in order to obtain a counting error of ±20% (95% confidence level) with a 2-liter sample at the 1 pCi/L level, about 2 hours of counting would be required. Although inconvenient, counting the sample repetitively over long periods gives one the option of examining the decay characteristics to evaluate if the net activity is decaying at the expected 6.14-hour half-life for ^{228}Ac (Fig. 4).

After counting, the final ^{228}Ra concentration, in pCi/L, is calculated from the equation:

$$^{228}\text{Ra (pCi / L)} = \frac{A}{2.22 \bullet E \bullet Y \bullet e^{-\lambda t_1} \bullet V} \bullet \frac{\lambda t_2}{1 - e^{-\lambda t_2}}$$

where,

A = net count rate (cpm);
E = counting efficiency expressed as a fraction (cpm/dpm);
Y = ^{133}Ba (Ra) yield expressed as a fraction;
V = sample volume (liters);
t_1 = decay time of ^{228}Ac, from start of rinse until start of counting (min);
t_2 = counting time (min); and
λ = decay constant of ^{228}Ac (1.88×10^{-3} min^{-1}).

The first decay correction, $e^{-\lambda t_1}$, corrects the measured activity back to the point of separation of ^{228}Ac from ^{228}Ra while the second correction, $\frac{\lambda t_2}{1 - e^{-\lambda t_2}}$, corrects for decay during counting. An additional correction is necessary if one desires to correct for decay of ^{228}Ra between sample collection and analysis.

We have determined the counting efficiency of our proportional counter for ^{228}Ac by running several ^{228}Ra solution standards directly through the columns, eluting Ac, and preparing the counting sources as normal. One may also choose to precipitate a known amount of ^{228}Ra with a very small quantity (<1.5 mg) of $BaSO_4$ and mount this on a filter. The counting efficiency may then be determined after appropriate correction for ingrowth of beta-particle-emitting daughters in the ^{228}Ra chain. We have managed to obtain comparable results this way and it has the benefit of the supported ^{228}Ac decaying with the longer ^{228}Ra half-life (5.75 yrs.). Since these two approaches produce efficiencies within our measurement error, the column yield and source preparation must be very close to 100%, i.e., the counting efficiency is not a combined term with corrections for other losses.

The reagent blanks we have run average about 0.16 cpm above background at FSU and about 0.75 cpm at EPI. In an earlier study (Burnett and Tai, 1992) we reported that there can be substantial differences in radium blanks depending upon the $BaCl_2$ reagent used for the carrier solution. Apparently, we have a lower-radium batch of barium chloride at FSU relative to EPI. For very low-level work, one could screen different batches of $BaCl_2$ before selecting one for use.

Another option for counting is to use a HPGe detector and monitor the 338- and 911-keV photopeaks of ^{228}Ac. While not nearly as sensitive as low-level beta counting, gamma-ray-spectrometry has the advantage of energy separation so interferences can be avoided. We have used successfully a 130-cc well-type germanium detector to count filters which have been rolled up into a small ball and placed in the bottom of plastic vials. Using the 911-keV photopeak with a 2-liter sample size, we can obtain an MDA of approximately 1 pCi/L after 6 hours of counting. A more favorable MDA is obtained using the 911-keV ^{228}Ac photopeak because it has a lower background than the 338-keV peak. The proportional counting approach is clearly more time efficient but gamma-ray-spectrometry is useful for higher activity samples or to evaluate possible interferences.

Examples of Results

In order to evaluate the effectiveness of the column separations, we conducted a series of decontamination experiments. After intentional addition of known amounts of potentially contaminating radionuclides and ^{228}Ra, the Ln·Spec™ separations were run and the source was sequentially counted overnight to evaluate the half-life. The first set of experiments consisted of adding 100 and 2000 dpm amounts of either ^{210}Pb or ^{90}Sr(^{90}Y) to a constant amount (~80 dpm) of ^{228}Ra. The results showed the expected half-life in each case and all sources returned to expected background count rates after sufficient time had passed for ^{228}Ac decay (**Table 1**). Another, more complex experiment involved the addition of several radionuclides (^{133}Ba, ^{207}Bi, and ^{210}Pb) to an EMSL "Performance Evaluation "B" (April 20, 1993) that already contained ^{90}Sr, ^{60}Co, ^{134}Cs, ^{137}Cs, ^{228}Ra, ^{226}Ra and daughters. This sample produced a half-life (6.03±0.23 hrs) within error of the known half-life but had a residual excess net count rate of approximately 0.1 cpm above the blank after 3 days of decay, indicating that a small quantity of a longer-lived radionuclide had been eluted with the ^{228}Ac. Considering the extreme contamination in this case, this small error seems acceptable.

We also analyzed a number of standard samples during the course of this research, including several interlaboratory comparisons distributed by EPA's Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas. An examination of these analyses (**Table 2**) shows that the results are within the experimental uncertainty at the 1σ level in most cases and all results agree with the expected values at the 95% (2σ) confidence interval. Although these evaluation samples are actually standards made up in deionized water, our experience after analyzing hundreds of natural water samples has been that matrix difficulties appear to be minimal. This is largely due to the co-precipitation step with $BaSO_4$ that reduces all samples to a common matrix from that point in the procedure.

An additional experiment was conducted on Performance Evaluation "A" (April 19, 1994) to ensure that one could evaluate the ^{226}Ra activity by collection of the effluent from the sample load and rinse. We collected these fractions from 3 runs of this sample and measured ^{226}Ra by the standard radon emanation method. After correction for radium loss via the ^{133}Ba recovery, we obtained an average result of 20.1±1.1 pCi/L, virtually identical to the EMSL value of 20.0±3.0 pCi/L. This illustrates a clear benefit of this methodology, i.e., two or more of the naturally-occurring isotopes of radium can be processed simultaneously.

SUMMARY

We have developed a procedure for determination of ^{228}Ra ($t_{1/2}$ = 5.75 y) in natural waters using the extraction chromatographic resins TRU·Spec™ and Ln·Spec™ to isolate the direct daughter product, ^{228}Ac, just before low-level counting. These separations are quantitative , simple, and relatively fast. The method also benefits from less waste generation than methods based on liquid-liquid extraction procedures. Elution curves and decontamination experiments show that actinium is not only completely separated from radium but also from elements such as lead, bismuth, and yttrium which could potentially interfere with the ^{228}Ac counting. The method is very amenable to a production mode of analysis and other isotopes of radium (^{223}Ra, ^{224}Ra, and ^{226}Ra) may be determined from the same preparation by appropriate modifications of the procedure.

ACKNOWLEDGMENTS

We thank Mike Fern, Susan Rajkovich and the staff at Eichrom Industries for their help and encouragement during the development of this technique. Reide Corbett and Michael Schultz of FSU and Terri Sherrill of EPI helped with some of the experiments reported here. Heyward Coleman, James Westmoreland, and others at EPI provided very helpful suggestions.

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BIOGRAPHIES

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Table 1. Half-life determinations of ^{228}Ac ($t_{1/2}$ = 6.14 h, Browne et al., 1988) from samples intentionally contaminated with potentially interferring radionuclides. These experiments were run at either Environmental Physics, Inc. (EPI) or Florida State University (FSU).

Experiment No.	Contaminating Nuclides	Experimentally Determined Half-life (hrs)
EPI-1[a]	^{90}Sr (^{90}Y) 100 dpm	6.09±0.23
EPI-2	^{90}Sr (^{90}Y) 2000 dpm	6.14±0.33
EPI-3	^{210}Pb (^{210}Bi) 100 dpm	6.10±0.19
EPI-4	^{210}Pb (^{210}Bi) 2000 dpm	6.09±0.30
FSU-1[b]	various 30-900 dpm	6.03±0.23

[a] Each EPI experiment contained approximately 80 dpm ^{228}Ra.

[b] FSU-1 decontamination experiment consisted of using approximately 800 mL of EMSL Performance Evaluation "B" (April 20, 1993) which contained the following nuclides: ^{90}Sr(^{90}Y) = 397 dpm; ^{60}Co = 466 dpm; ^{134}Cs = 31 dpm; ^{137}Cs = 438 dpm; and ^{226}Ra = 213 dpm. In addition, we added approximately 8000 dpm ^{133}Ba, 900 dpm ^{207}Bi, 500 dpm ^{210}Pb, and 65.9 dpm ^{228}Ra.

Table 2. A few examples of ^{228}Ra analysis of known samples by extraction chromatographic resins. FSU results given at the 1σ level based on counting statistics.

Sample	Expected Results pCi/l	FSU Result pCi/L	Method
EMSL Ra in Water July 17, 1992	16.7 ± 3.3	16.3 ± 0.3 17.6 ± 0.7	TRU·Spec™ Ln·Spec™
EMSL Performance Evaluation "A" April 20, 1993	19.0 ± 3.1	20.6 ± 0.7	TRU·Spec™
EMSL Standard ^{228}Ra solution			
(1) load directly into column	59.3 ± 2.1	60.6 ± 1.4	Ln·Spec™
(2) add to 0.5 L DDW, full process		58.0 ± 1.3	
Decontamination Experiment FSU-1[a]	29.7 ± 1.0	31.7 ± 0.5	Ln·Spec™
EMSL Performance Evaluation "A" April 19, 1994[b]	20.1 ± 5.0	21.6 ± 1.2	Ln·Spec™

[a] See footnote in Table 1 and text for description.

[b] Ra-226 was analyzed via radon emanation by collection of the sample load and rinse from the Ln·Spec™ column. Our result of 20.1±1.1 pCi/L compares very well to the expected result of 20.0±3.0 pCi/L.

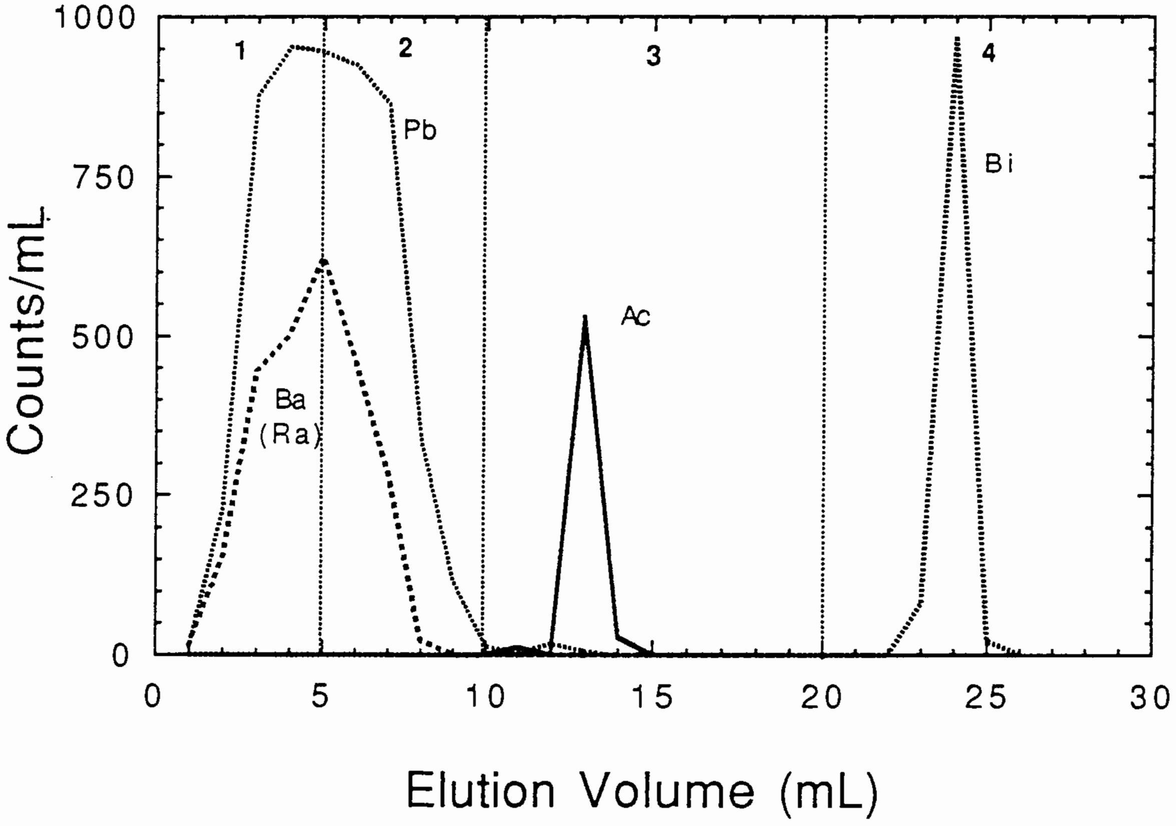
FIGURE CAPTIONS

Figure 1. Elution curves for barium (^{133}Ba), actinium (^{228}Ac), and bismuth (^{207}Bi) from a TRU·Spec™ column. The numbering sequence corresponds to the following: (1) sample load in 2M HNO_3; (2) rinse with 2M HNO_3; (3) Ac elution with 1M HCl; and (4) Bi elution with 6M HCl.

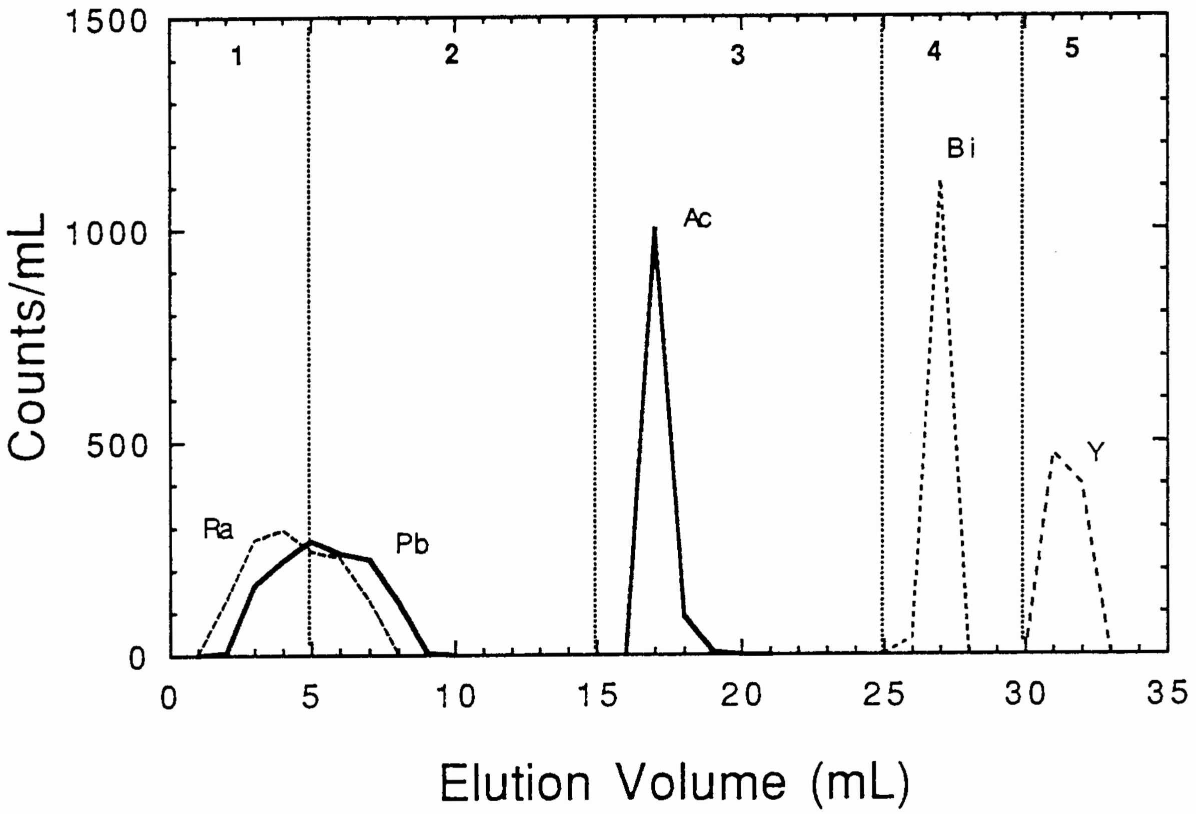
Figure 2. Elution curves for radium (^{226}Ra), lead (^{212}Pb), actinium (^{228}Ac), bismuth (^{207}Bi), and yttrium (^{88}Y) from a Ln·Spec™ column. The numbering sequence corresponds to the following: (1) sample load in 0.09M HNO_3; (2) rinse with 0.09M HNO_3; (3) Ac elution with 0.35M HNO_3; (4) Bi elution with 2M HNO_3-0.1M oxalic acid; and (5) Y elution with 3M HCl.

Figure 3. Generalized flow chart for the Ln·Spec™ method for separation of actinium from radium. Ba-133 is used as a yield tracer for radium through the precipitation and metathesizing processes which may not be strictly quantitative. Ac-228 is separated on the Ln·Spec™ resin after ingrowth from ^{228}Ra, preconcentrated by $BaSO_4$ precipitation.

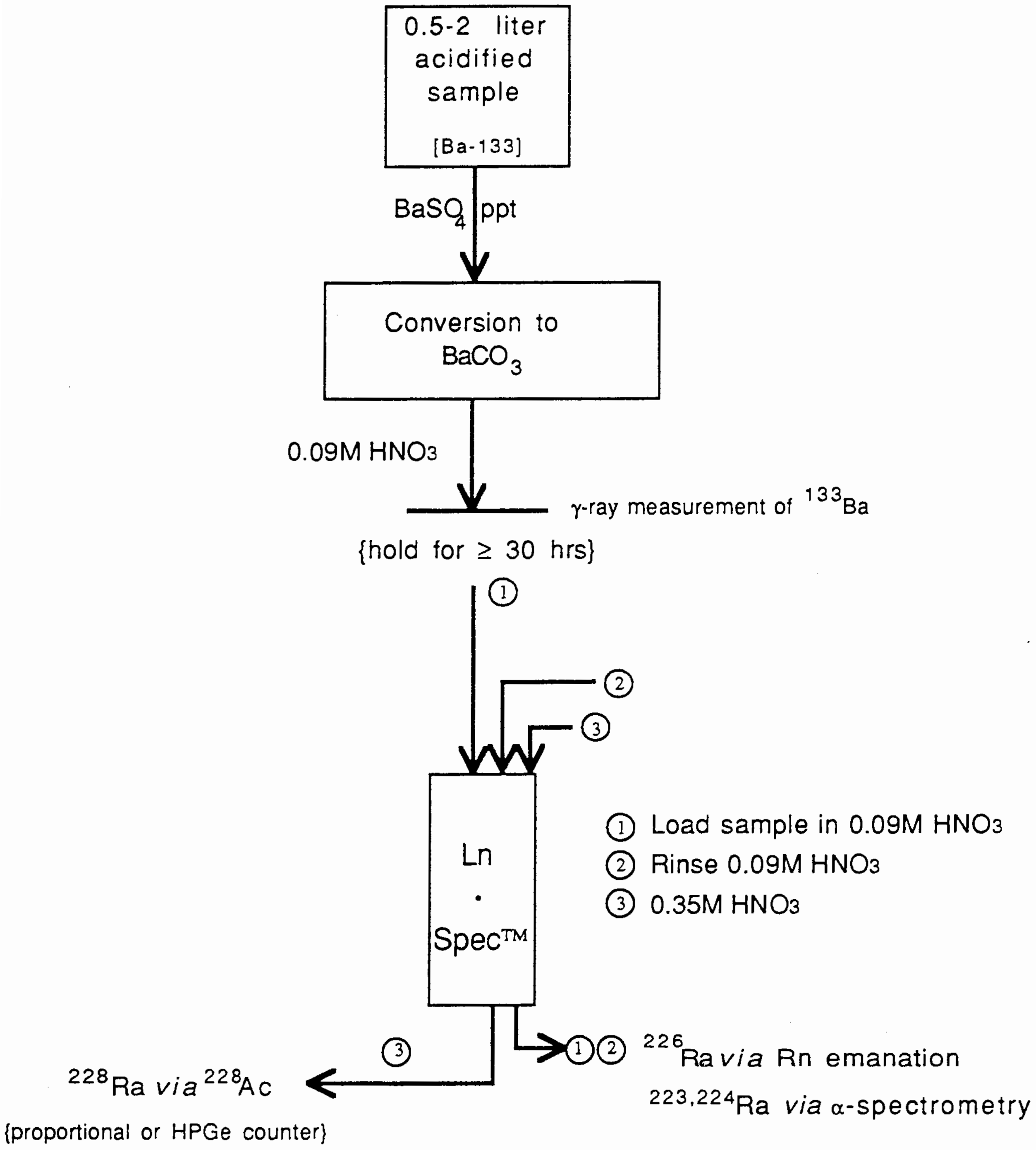
Figure 4. Decay curve produced by sequential counting of a ^{228}Ra sample. The calculated half-life is within experimental error of the known half-life for ^{228}Ac (6.14 hrs.).



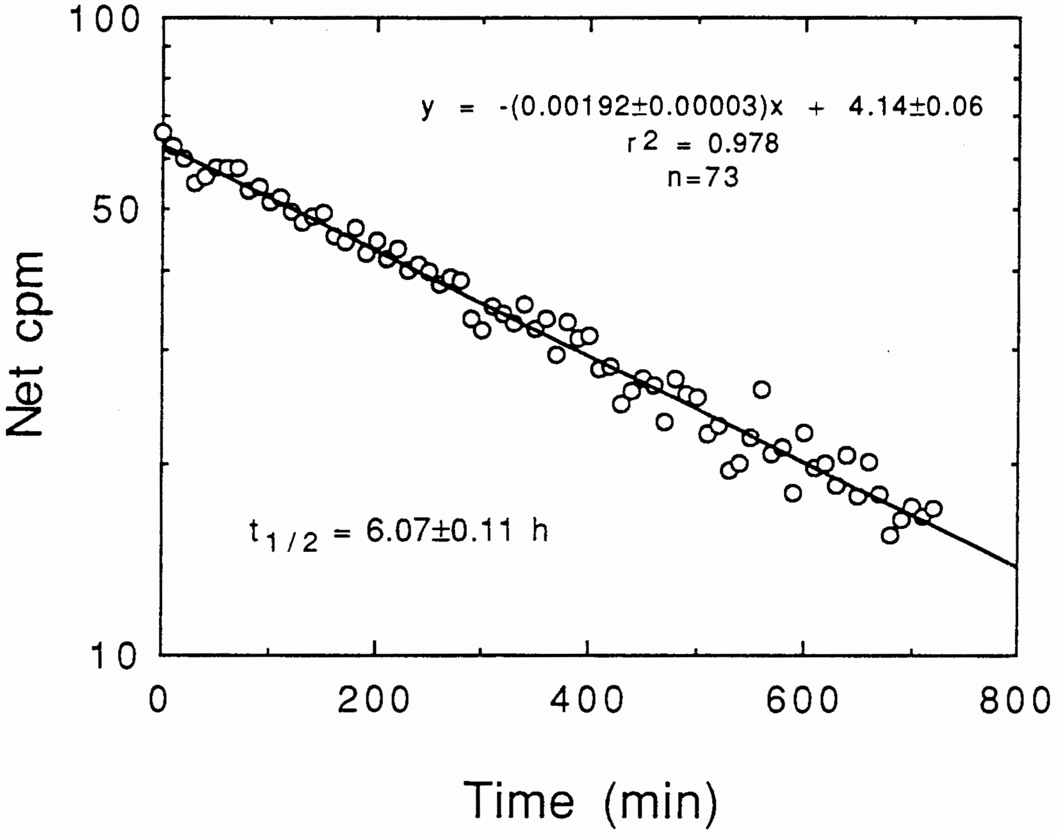
wc burnett Fig. 1



wc burnett Fig. 2



wc burnett Fig. 3



wc burnett Fig. 4