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January 13, 1987

Mr. Stephen Billets
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Dear Mr. Billets,

The first quarterly report of the project "Screening Method for Radium-228 in Drinking Water" is enclosed. On the basis of our earlier discussions, we await comment by you or other EPA staff to select for preliminary testing the most promising methods. Please note that we have described four methods in the Appendix according to the format presented in our project proposal.

I am looking forward to hearing from you.

Sincerely yours,

Bernd Kahn

BK/rs

cc: Chungking Liu, EMSL/EPA
Reports Coordinator, OCA E-25-M16

Screening Method for Radium-228 in Drinking Water
Report of First Quarter
Oct. 10, 1986 - Jan. 10, 1987

Introduction

The initial step in selecting a radium-228 screening method was to survey the literature for radium-228 procedures that could be adapted for screening. The available procedures were considered according to previously specified criteria. Four possibilities are presented in a uniform format for comments by US EPA staff. The preferred approaches will be considered in further detail by determining some factors that are currently uncertain.

Literature review of radium-228 analyses

The chemical literature from January, 1980 to June, 1986 was reviewed to collect the analytical procedures for radium-228 listed in the bibliography. Methods published before May, 1980 were compiled by Noyce (1981).

The approved radium-228 method for the National Interim Primary Drinking Water Regulations, updated by Krieger and Whittaker (1980), consists of precipitating sulfates from a 1-liter sample and then separating actinium-228 and counting its beta particles with a low-background proportional or Geiger-Mueller detector. It is a long and involved procedure. The method by Baratta and Lumsden (1982) also separates actinium-228 and counts it with a gas-filled detector, but uses different purification steps.

Liquid scintillation counting after radiochemical separation is used in a newer EPA procedure by Velten and Jacobs (1983). Liquid scintillation counting permits measurement of the weak beta particles emitted by radium-228. The lengthy purification procedure eliminates interferences from other low-energy beta particles and includes direct uptake of the radium into the organic scintillation solvent for relatively high counting efficiency. Another approach, by Godoy and Schuettelkopf (1983), measures Cherenkov radiation in water from the high-energy actinium-228 beta particles after suitable chemical purification. Organic solvent and scintillator are not needed with the liquid scintillation counter in this procedure.

Gamma-ray spectral analysis of actinium-228 and subsequent progeny such as thallium-208 is an attractive option because little or no chemical separation is needed; radium-228 is both identified and quantified by the characteristic gamma rays of its progeny. One approach (Moore, 1984; Michel, King, and Moore, 1981) collects radium from water samples of several liters on MnO₂-impregnated fibers in an absorption column, and counts with

a Ge(Li) detector after actinium-228 ingrowth. Radium-226 can be determined simultaneously by measuring the characteristic gamma rays of its progeny. Sulfate precipitation (Bivens, 1986) is an alternative for collecting radium. Gamma-ray spectral analysis has also been used by Martin (1985) as part of multiple-radionuclide analysis and by Noyce et al. (1983) for calibrating radium-228.

McCurdy and Mellor (1981) use coincidence counting of gamma rays and alpha or beta particles. Radium is collected from the water sample by sulfate precipitation. Sets of photomultiplier tubes detect the light from zinc sulfide stimulated by alpha particles, from a plastic scintillator stimulated by beta particles, and from thallium-activated sodium iodide stimulated by gamma rays. The method utilizes gamma-ray spectrometry to maintain a very low background and minimize interference from other radionuclides that may precipitate with sulfates.

The survey by Blanchard et al. (1985) of analytical methods for the Regulations recommends a new screening procedure for radium-228 in place of gross-alpha-particle measurement followed by radium-226 analysis. It suggests consideration of gross-beta-particle measurement or a radium-228 analytical method at an acceptable level of effort and cost.

Consideration of radium-228 screening method

Various approaches for screening water samples for the presence of radium-228 at concentrations that can contribute to exceeding the MCL for radium are being considered. A first set of possible methods is described in Appendix A in a uniform format. The following criteria are applied to each method:

1. Applicability of currently specified sample collection and initial treatment, including current sample volumes and typical time intervals.
2. Applicability of radiation detection equipment commonly available in radiometric laboratory.
3. Applicability of common skills for radiochemical analysis.
4. Time and costs comparable to current screening method requirements.
5. The 1.96-sigma value to be 1 pCi/l at the radium-228 concentration of 5 pCi/l, and the detection limit to be 1 pCi/l.
6. False positive results due to interferring radionuclides not to exceed the rate of false positives with the current screening method.

7. False negative results to be limited by the standard deviation value at 1 pCi/l.

The screening methods derive from the recently published procedures or recommendations presented in the preceding section.

The gross beta method is taken as a point of departure because, if appropriate, it would utilize the same sample as the gross alpha method and the same proportional counter, set at a higher voltage to detect beta particles. As indicated in the Appendix A review, a 200-minute counting time would be expected to attain the specified detection limit, and a 2-day ingrowth time for actinium-228 is needed. Brief tests are needed to examine realistically the interferences from radium-226 daughters and other beta-particle emitters. Even if data interpretation based only on gross alpha and beta particle activities is highly uncertain, it is possible that some combination of the two values can give a definite indication that radium-226 and radium-228 analyses are needed.

Sulfate precipitation is an alternative to evaporating a 200-ml sample that has already been considered by EPA. This method provides a uniform sample instead of one that has a variable dissolved solid content which affects the alpha- and beta-particle count rates. It also eliminates some -- although not all -- radioactive contaminants, and may be particularly useful for gross beta counting in removing potassium-40. Because dissolved solids are eliminated, a larger sample (e.g., 1 liter) can be used to obtain the higher count rates that yield better counting statistics, lower detection limits, or shorter counting periods. Precipitating barium or lead sulfate and collecting the precipitate require more effort and skill than is needed for evaporating water, but are not difficult. The same complexity discussed above for gross beta counting occurs if radium-226 and radium-228 are both present.

Instead of the low-background proportional counter, a liquid scintillation counter could be used for both gross alpha and gross beta particle measurements. These detectors, generally with automatic sampler changers and three energy windows, are widely used. The sample could be prepared, as above, either by evaporation or sulfate precipitation. The pattern of alpha and beta count rates as function of channel settings needs to be considered to determine whether radium can be screened with this detector at the desired concentrations. A number of alternatives in counting -- low energy radium-228 vs. high energy actinium-228, all water vs. all solvent for counting, additional purification or timed measurement -- should be explored.

Use of a Ge(Li) detector with gamma-ray spectrometer could be a major advance. Because the sample is analyzed directly for radium content, no radium screening is needed. The counting efficiency of the detector for gamma rays, however, is generally lower than that of the proportional or liquid scintillation

counters for alpha and beta particles, hence, a larger sample is needed, possibly 3 liters. Several volume reduction steps are possible, including evaporation, precipitation or surface adsorption. The method would also detect many man-made radionuclides that emit gamma rays, but would not detect uranium or thorium, as is done by the currently used gross alpha particle screening. Gamma ray detectors and spectrometers are widely available in radioanalytical laboratories, but the desirable feature of having an automatic sampler changer is not as common.

Coincidence counting has not been considered in this first round of evaluations because such detectors are believed to be relatively specialized instruments, not commonly used in radioanalytical laboratories. Alternatives to sulfate precipitation or more lengthy purification procedures have also not been considered to keep the procedure relatively simple and familiar to the analyst, who currently uses sulfate precipitation for radium analysis.

Summary and discussion of future work

Several methods for radium-228 screening appear to be feasible within the proposed criteria. Subject to response by EPA staff, we will perform experiments with the procedures of choice to check their feasibility regarding such factors as detection limits, interferences, and ease of analysis. We recommend that EPA select more than one method to avoid discarding promising methods at this early stage. We will also consider other methods that appear promising to EPA staff.

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Appendix A
Potential Screening Methods

Procedure: Gross Beta Particle Analysis

Brief description: Evaporate 200-ml sample to dryness in planchet. Flame. Weigh sample to obtain self absorption factor. Count 100 minutes in low-background beta counter (proportional or G-M).

Assumptions: Counting efficiency 38%; background 1.2 count/min, measured 400 min; self absorption factor 0.90.

Detection limit: 1.6 pCi/l (1.96 sigma)

Evaluation:

- (1) required skill: On par with existing gross alpha particle activity measurement.
- (2) required effort: Use sample prepared for gross alpha particle activity measurement.
- (3) required equipment: Same as for gross alpha particle activity. Current utilization at, say, 500 water sample measurements per year (including background and quality control) is 1,000 minutes/week. At availability (overnight and over weekend) of 7,400 min/week, available detection equipment can be used for this method.
- (4) appropriate detection limit: If detection limit of 1 pCi/l is required, the counting period can be doubled to meet limit.
- (5) false negatives: The beta particle activity that is measured is actinium-228, hence one must determine if this radionuclide remains dissolved in the water sample. If not, an ingrowth period of 1.5 day is required between sample preparation and counting for actinium-228 to accumulate from radium-228 decay.
- (6) false positives:
 - (a) If radium-226 is in the sample, lead-214 and bismuth-214 either may be in the sample or may grow into it with 3.8-day radon-222. This factor must be checked. Some level of these beta-particle emitters is acceptable since the presence of radium-226 at above 5 pCi/l in any case exceeds the MDL.

- (b) The impact of K-40 must be checked. The beta particle activity of potassium is 0.74 pCi/mg. Typical water supplies have potassium levels of 1 mg/l, and some ground-water supplies have much higher levels.
 - (c) Long-lived radionuclides that emit beta particles due to other natural decay chains are believed to be only occasional contaminants in the water, but this needs to be checked.
 - (d) No man-made radionuclides are believed to be present as interferences except under extraordinary conditions.
 - (e) Short-lived radionuclides from the radium-228 decay chain beyond thorium-228, i.e. lead-212 and thallium-208, may be present in the sample and may require a time interval for decay of 2 days before counting. This needs evaluation, because these radionuclides at high levels may be simply another indication of the presence of radium-228.
 - (f) Some samples contain excessive dissolved solids that limit the sample volume that can be used to avoid excessive self absorption of beta particles. The extent of this problem needs to be evaluated, but it has not invalidated the gross alpha particle screening method.
- (7) non-reproducible conditions:
- (a) If radium-224 had been present, beta particles emitted by lead-212, bismuth-212, and thallium-208 daughters may be counted until they have decayed. This can be avoided by waiting until several radium-224 half lives have passed between sample collection and counting.
 - (b) If radium-228 beta particles are detected, the count rate is very dependent on the fraction of unabsorbed weak beta particles. This can be avoided by inserting an absorber for all radium-228 beta particles.
 - (c) If radium-226 is present, the beta-particle count rate will depend on the time for radon-222 ingrowth and the fraction of radon-222 remaining in the sample. Some of this uncertainty may be acceptable, as indicated in (6) (a), above.

Conclusion prior to testing: Method is potentially feasible but requires evaluation of the items indicated above. Particular advantage is that the sample previously prepared for gross alpha particle would be counted; major disadvantages may be interference from radium-226 daughters or potassium-40.

Procedure: Proportional-counter Measurement of BaSO₄ Beta-particle Activity.

Brief description: Precipitate barium sulfate from 0.5-liter sample. Collect precipitate on filter. Count in low-background detector.

Assumptions: Counting efficiency 38%; background 1.2 count /min., measured 400 min.; self absorption factor 0.90.

Detection limit: 0.7 pCi/l (1.96 sigma)

Evaluation:

- (1) required skill: Analytical - easier than current radium-228 analysis; radiometric - on par with current gross alpha particle measurement.
- (2) required effort: Precipitate and filter sample.
- (3) required equipment: Same as for gross alpha particle activity. Current utilization at 10 samples/week (500 per year) including background and quality control, the detector will be used for 1,000 min./week out of 10,000 minutes.
- (4) appropriate detection limit: Suitable for limit of 1 pCi/l with smaller sample (0.4 l) or shorter counting period.
- (5) false negatives:
 - (a) Ingrowth of Ac-228, the radionuclide that is counted, requires 2 days.
 - (b) Radium precipitation and collection must be quantitative.
- (6) false positives
 - (a) Ra-226 daughters that emit beta particles (Pb-214 and Bi-214) will be counted if Ra-226 is in the sample.
 - (b) Other radionuclides that have insoluble sulfates -- for example, barium, strontium and lead -- and emit beta particles will be counted. Barium sulfate may also carry some other radionuclides.

- (c) Alpha particles may be partially detected by the beta-particle detector despite pulse height discrimination.
- (7) Non-reproducible conditions
- (a) If Ra-224 is present, its daughters may be counted for a number of Ra-224 half lives.
 - (b) If Ra-228 beta particles are also detected, the count rate is dependent on the attenuation characteristics of the precipitate.
 - (c) If Ra-226 is present, the alpha and beta particle count rate depends on Rn-222 ingrowth, i.e., increases over a 1-month period.

Alternatives:

- (1) An alternative precipitation agent or additional purification steps may be used to remove non-radium radionuclides.
- (2) Multiple count rates for shorter counting periods (e.g. two 50-min counts at selected times after precipitation) may be used with a larger sample volume to distinguish between Ra-228 and Ra-226.

Conclusion prior to testing: Method is potentially feasible but requires evaluation of the items indicated above. The advantages of the procedure are partial removal of interferences by means of precipitation and maintaining identical beta-particle attenuation. The major disadvantage is the potential multiple sources of count rate from the 3 radium isotopes. The latter may not be an overwhelming problem because the presence of any radium activity above a certain level will, in any case, indicate that the MCL has been exceeded.

Procedure: Liquid Scintillation Counting

Brief description: Precipitate barium sulfate from 1.5 liter sample. Let settle and collect precipitate by filtering or centrifuging. Dissolve in 10 ml EDTA solution. Mix with 10 ml LS cocktail and count 100 minutes in LS counter.

Assumptions: Counting efficiency for Ra-228 beta particles (55-keV maximum energy) in tritium channel is 33%; background of 21 counts/min is measured 400 minutes.

Detection limit: 1.0 pCi/l (1.96 sigma)

Evaluation:

- (1) required skill: Analytical-easier than current radium-226 analysis; radiometric - same as measurement of tritium required in Section 141.16 of the NIPDW Regulations.
- (2) required effort: Collect precipitate from large-volume sample. Dissolve precipitate and mix solution with solvent.
- (3) required equipment: Liquid scintillation counter with several windows for energy discrimination and automatic sample changer. At average rate of 10 samples per week (500 per year) including background and quality control measurements, the detector will be used for 1,000 minutes out of 10,000 minutes.
- (4) appropriate detection limit: Suitable for limit of 1 pCi/l. For 1-l samples, 220-min. counting periods would be required.
- (5) false negatives: No potential problem is obvious.
- (6) false positives:
 - (a) Corrections must be made for low-energy beta particles from higher-energy groups emitted by Ra-228 daughters and for low-energy conversion electrons and alpha particles. Similar corrections are necessary for short lived Ra-226 daughters. Corrections must be determined on basis of ratios of count rates in several channels.
 - (b) Lead-210 (22-yr half life) interferes because it emits 17-keV maximum (80%) and 61-keV maximum

(20%) beta particles and precipitates with barium sulfate.

(7) non-reproducible conditions:

- (a) Ingrowth and decay by daughters of Ra-228 and Ra-226 will change extent of interference from other radionuclides in tritium channel.
- (b) Presence of air space may introduce irregularities in spatial distribution of radon and daughters.

Alternatives:

- (1) More extensive chemical separation to remove Pb-210. Selective precipitation of barium sulfate in the presence of lead sulfate is performed with EDTA at a selected pH value.
- (2) Chemical processing to dissolve radium in scintillation solution. This procedure increases counting efficiency so that 1-1 sample can be used with 100-min. counting period.
- (3) Use count rates in higher-energy channels. This procedure increases the counting efficiency considerably but complicates data interpretation due to interferences from Ra-226 and daughters.
- (4) Use Cherenkov counting. The scintillation solution is eliminated, doubling the sample volume. The high energy beta particle group from Ac-228 is measured, hence counting should be performed after Ac-228 reaches equilibrium with Ra-228 after 2 days. Only high-energy beta particles interfere, e.g. Bi-214 in the Ra-226 chain.

Conclusion prior to testing: Method is potentially feasible but requires evaluation of the items indicated above. Its advantage is that it can be used for determining Ra-228 directly. Radium-226 and daughters, and possibly some other radionuclides that accompany BaSO₄ may interfere, but corrections based on Ra-226 analysis, channel ratios, or ingrowth-decay patterns may be possible.

Procedure:**Gamma-ray Spectral Analysis****Brief Description:**

Precipitate barium sulfate from 3 liter sample. Let settle and collect precipitate by filtering or centrifuging. Count 100 minutes with Ge(Li) detector and spectrometer.

Assumptions:

Counting efficiency (combined intrinsic efficiency and geometry) of 911-keV Ac-228 (29%) is 3% and of 583-keV Tl-208(30%) is 4%; for 352-keV Pb-214 (35%) it is 7% and for 609-keV Bi-214 (43%) it is 4%. The background in count/min is 0.07 (911 keV), 0.2 (583 keV), 0.3 (352 keV) and 0.2 (609 keV); it is measured once per week for 3,600 min.

Detection limit:

Ra-228 (911 keV) 1.0 pCi/l (1.96 sigma)
(583 keV) 1.2
Ra-226 (609 keV) 0.8
(352 keV) 0.7

Evaluation:

- (1) required skill: Analytical - easier than current radium -226 analysis; radiometric - same as measurement of photon radioactivity required in NIPDW Regulations.
- (2) required effort: Collect precipitate from large-volume sample. Perform gamma-ray spectral analysis. Interpret complex gamma-ray spectrum.
- (3) required equipment: Gamma-ray spectrometer, including Ge(Li) detector with at least 15% efficiency (nominal, relative to NaI(Tl) detector at 1.3 MeV). For 500 water sample measurements per year (including quality control), load of 10 samples/week x 100 minutes/sample can be handled during three 8-hour shifts per week.
- (4) appropriate detection limit: Suitable for limit of 1 pCi/l. Longer counting periods can be used for less efficient detectors or higher background count rates from radium.
- (5) false negatives: (a) Radium daughters are measured, hence these daughters must be in equilibrium with radium. Ingrowth time is 2 days for Ac-228 and 3 days for Tl-208. If Ra-226 is to be measured, ingrowth time is 1 month, or ingrowth

correction is required (and detection limit becomes higher).

- (b) Radium precipitation and filtration must be quantitative or must be corrected for yield.
 - (c) Absence of significant radon emanation from the precipitate must be confirmed for Tl-208 and for Ra-226 daughters.
- (6) false positives: Initial sulfate separation and spectral analysis with confirmatory measurements of two or more photons per radium isotope minimizes erroneously counting gamma rays from other radionuclides.
- (7) non-reproducible conditions
- (a) Impurities in the water sample may affect radium precipitation yield.
 - (b) Fluctuating radon levels in counting-room air may affect the background count rate at the characteristic photon energies.
 - (c) Any photon-emitting radionuclide at relatively high concentrations in the precipitate may increase the radium detection limit.

Alternatives:

- (1) Absorption of radium on MnO₂-impregnated fibers. Collection of radium from water sample is simplified. Information on medium preparation, fractional recovery, retention of radon and interferences can be obtained from Moore (1984).
- (2) Sample evaporation. Reduction of volume from 3 l to 50 ml is a simple procedure. Two-fold lower counting efficiency must be compensated for by four-fold longer counting period. If Tl-208 and Ra-226 daughters are to be counted, sample must be sealed to avoid radon emanation, and container must be full. All potentially interfering radionuclide will be present.

Conclusion prior to testing. Method is potentially feasible but requires evaluation of the items indicated above. Particular advantage is that screening and analysis are combined for Ra-226 and Ra-228; major disadvantage is that radionuclides that do not emit many photons -- i.e. uranium and thorium -- are not detected.



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May 19, 1987

Dr. Chung King Liu
Nuclear Radiation Assessment Division
EMSL/US EPA
P.O. Box 15027
Las Vegas NV 89114

Dear Dr. Liu:

The report for the second quarter of the project "Screening Method for Radium-228 in Drinking Water" is enclosed. We have taken the three potential screening methods that you selected from the recommendations in our first quarterly report and have tested initial radium coprecipitation with barium sulfate and determined the counting efficiency with a Ge(Li) gamma-ray spectrometer, a proportional counter for alpha and beta particles, and a liquid scintillation counter for alpha and beta particles. A graduate student worked 1/3rd time on this project for the quarter.

Best regards.

Sincerely yours,

Bernd Kahn

BK/rs

Enclosure

Screening Method for Radium-228 in Drinking Water
Report for Second Quarter
Jan. 10 - April 10, 1987

Introduction

Three of the four potentially useful methods for radium-228 screening identified in the first quarterly report were recommended for further study by the program officer, Dr. Chung King Liu, During his site visit on Feb. 3, 1987. All three methods require collection of radium -- for example, by coprecipitation with barium sulfate, but utilize different radiation detection procedures. The three procedures consist of (1) gamma-ray spectrometry with a Ge(Li) or Ge detector, (2) gross beta particle counting with a gas-filled detector, and (3) liquid scintillation (LS) counting in a 3-channel system. During this second quarter, initial tests were performed to determine the chemical yield of the barium sulfate precipitation for the sample volumes that were estimated to be needed for detecting as little radium-228 as 1 picocurie per liter (pCi/l). In addition, elevated levels of radium-228 tracer were precipitated with barium sulfate and then counted by the three procedures to establish the counting efficiency -- and hence, detection limits -- for radium-228 and its radioactive progeny. The same procedure was performed for radium-226 to determine the extent of potential interference and the possibility of simultaneous measurement where appropriate.

Precipitation Yields for Radium Coprecipitation

The initial portion of the EPA Radium-226 Radon Emanation Technique (Appendix A, steps 8.1 and 8.2) was used to precipitate barium sulfate for radium coprecipitation, determining the chemical yield for various water volumes and quality. Initial estimates of the detection sensitivity for radium-228 by the three counting procedures suggested that 0.5, 1.5 and 3 liters of sample were needed for the different procedures.

After precipitating barium sulfate as described in the EPA method and letting the precipitate settle overnight, the entire sample was filtered through a 47-mm dia. filter to collect barium sulfate. Either a glass fiber filter (Gelman type A/E) or a membrane filter (Gelman Metrical, 0.45um) was used. The precipitate was rinsed with 100 ml water, dried overnight at 105° C, and weighed. The added barium sulfate was found to yield 28.3 mg when completely recovered. The test waters were 0.5, 1.0, and 3.0 liters of deionized water and 3.0 liters of Atlanta tap water.

The results of 39 tests summarized in Table 1 show an average chemical yield of about 95 percent for 0.5 and 1.0 liter of deionized water, with a relatively consistent recovery

indicated by the 1 - 2 percent standard deviation (SD). The yield decreased significantly at higher volumes and was even lower when tap water was substituted for demineralized water.

In practice, the radioactivity measurements would be corrected for chemical yield to determine the radium-228 concentration in water, and yields as low as 73 percent appear to be acceptable. However, it is desirable to understand the reasons for the decreased yields and to improve these yields where possible. A more detailed examination of the barium sulfate precipitation procedure, therefore, is planned.

Another EPA procedure which combines barium sulfate, iron hydroxide, and paper pulp (see Appendix B) to obtain a consistent amount of precipitate was also tested. The precipitate carries a much wider range of radionuclides than barium sulfate by itself. Its advantages include carrying some additional radium progeny for increasing the detection sensitivity, and maintaining a more uniform precipitate so that a constant correction for alpha and beta particle self absorption can be applied. Its disadvantage is reduced decontamination from interferences.

Two samples of deionized water, one of 0.5 liter and one of 3.0 liters, both resulted in a precipitate that weighed 21.4 mg (oven dried overnight at 105° C). The percent yield will have to be determined and additional tests will be performed to examine the effect of water volume and quality.

Counting Sensitivity for Radium-228 Tracer

Radium-228 tracer in water was coprecipitated with barium sulfate, collected on a filter, and counted with each of the three radiation detectors considered for this procedure. The net count rate per pCi radium-228 tracer was calculated for each system in order to estimate the sample volume required to reach a detection limit of 1 pCi/l. The precipitates were counted at various time intervals after precipitation to observe the influence of radioactive progeny ingrowth and decay. The background count rates at the counting settings were also determined for calculating the detection limit.

The procedure consisted of adding 430 pCi radium-228 to 0.5 l tap and precipitating, filtering, and weighing barium sulfate as described above. One modification was drying with alcohol and ether washes in order to weigh and count within an hour of filtering. Three samples were processed in parallel to obtain a sample for each counting procedure. All three filters were counted initially in 5-cm steel planchets with a gas-flow proportional anti-coincidence counter for alpha and beta particle activity to compare count rates.

The chemical yield of the samples was between 90 and 97 percent and all counting results were corrected for this yield. The count rates of the three samples were consistent. One of the

two samples collected on glass fiber filters was then counted with the Ge(Li) detector and the other with the proportional counter. The third sample, which had been collected on a membrane filter, was separated from the filter for counting in a liquid scintillation detector. The separation consisted of dissolving the filter with 15 ml concentrated nitric acid, centrifuging and decanting the solution, dissolving the barium sulfate in 13 ml 0.25 M disodium EDTA plus 2 drops ammonium hydroxide while heating, transferring the solution (reduced to 10 ml) to a glass LS counting vial, adding 11 ml scintillation cocktail (PPO)/MSB/Triton/p-xylene) and mixing the solutions thoroughly.

The following detectors were used:

(1) Ge(Li), nominal 25 percent efficiency, shielded in 10 cm lead, with power supply, amplifier, and multichannel analyzer system (Canberra).

(2) Gas-flow proportional counter, 0.08 mg/cm² end window, with anti-coincidence system, pulse-height discrimination to separate alpha and beta particle pulses, 10 cm lead shielding, automatic sample changer (Tennelec LB 5100).

(3) Liquid scintillation counter, with 3-channel pulse height discrimination, 5 cm lead shielding, automatic sample changer (Beckman LS-233).

The samples were measured for 2,000- or 10,000-second periods with the gamma-ray spectrometer, for 10-minute periods with the proportional counter, and for 50-minute periods with the LS counter. Backgrounds were measured repeatedly for the same periods with the proportional and LS counters, and for 200,000 seconds over the weekend for the gamma-ray spectrometer.

The net count rates per pCi radium-228 that were observed are given in Table 2 for the three detector systems, together with the pertinent background count rates. The 2-standard-deviation value of the gross count rate per pCi (i.e., net plus background) for a 100-minute count was calculated for the last column in Table 2 to indicate the sensitivity of the counting system. The standard deviation of the background count rate must also be included in the calculation because the background must be subtracted, but this standard deviation value can be minimized by lengthy or repeated background measurements. The required sample volume, in liters, is somewhat larger than the 2 SD value divided by the net count rate in Table 2.

The results in Table 2 suggest that a 3-liter sample is required for gamma-ray spectrometry, as estimated in the initial method evaluation. The two other systems require less than 0.5 liter, which is less than estimated in the initial method evaluation. As indicated below, however, these samples include

radium-224 and radioactive progeny that would generally not be present.

The Ge(Li) measurements of the 911- and 338-keV gamma rays of the 6.13-hr actinium-228 daughter of radium-228 showed constant values, equal to the amount of radium-228 tracer, in four measurements spaced from 1 hour to 4 days after the barium sulfate precipitation. The measurements indicate that, within the 10 percent measurement uncertainty, actinium is coprecipitated completely with barium sulfate. On the other hand, lead-212 (238 keV) and bismuth-212 (727 keV) were only approximately two-thirds of the actinium-228 activity after 1 hour, were approximately equal to it after 1 day, and then decreased during the next 7 days. The activity of thallium-208 (583 keV) was approximately one-half of the activity of actinium-228 in all four measurements. These observations suggest that lead is partially carried by barium sulfate and that thorium may be partially or not at all carried. To the extent that thorium-228 is missing, lead-212 and its progeny decay with the 3.6-d half life of radium-224.

The gross alpha and beta particle activity measurements, performed at half-hour intervals from 1 to 27 hours after precipitation, showed a constant alpha particle count rate over this period, while the beta particle count rate increased by 20 percent to a maximum after 13 hours and remained at that value for the next 14 hours. The count rates had decreased by about 20 percent for alpha particles and 10 percent for beta particles by the next set of measurements, taken 6 days after precipitation, and had decreased by about 50 percent of the original for alpha particles and 30 percent for beta particles after 29 days. These changes support the above inference concerning lead coprecipitation, and also suggest that approximately one-half of the thorium coprecipitated on barium sulfate.

The measurement results with the LS counter, taken 5 hours after separation, give the value shown in Table 2. Unfortunately, periodic malfunction of the detector yielded questionable values during subsequent measurements. Because the detector combines alpha and beta particles count rates as used over the full energy spectrum range (all windows combined over the range 0 - 10), a slight increase in count rate would be expected during the next 8 hours after the indicated measurement. A preliminary spectrum measurement also suggest that energy discrimination, selecting the range 3 - 8, may retain about 90 percent of the net radium-228 plus progeny count rate while eliminating one-half of the background.

The same information as for radium-228 is presented in Table 2 for radium-226, showing that radium-226 is detected with somewhat lesser sensitivity in all three systems. A major difference is due to the 54-second half life of radon-220 compared to the 3.82-day half life of radon-222. Hence, all short-lived progeny of radium-226 must either be counted within a

few minutes after separation or will require ingrowth of radon-222 before they can again be seen at concentrations comparable to those of radium-226. The tracer consisted of 480 pCi radium-226 from an old standard solution, and was used as described for radium-228.

Further measurements are required to confirm the LS values and to check the predicted detection limits. The limits must also be adjusted for the partial or complete absence of radium-224 in radium-228 analysis, because the standard used contains radium-224 in equilibrium. A similar consideration applies to long-lived lead-210 with bismuth-210 and polonium-210 progeny in the radium-226 standard but not in the usual samples. Noteparticularly that a sample limited to radium-228 and actinium-228 will not have any alpha particle activity.

Summary and Discussion of Future Work

The research undertaken during the second quarter of the project provides an indication of the chemical yield expected from barium sulfate coprecipitation of water samples in the 0.5 - 3.0-liter range predicted as necessary to obtain a detection limit for radium-228 of 1 pCi/l. Tests with a mixed barium sulfate-iron hydroxide precipitate were also begun.

A set of tracer radium-228 solutions precipitated with barium sulfate were counted with the three detection systems that are being considered to determine, on the basis of detection efficiency and background count rates, the volume of sample required to reach the detection limit. The detection limits equalled or exceeded those predicted earlier, but the tracers include radioactive progeny in equilibrium with radium-228, and the barium sulfate was found to carry significant fractions of thorium and lead radionuclides, which may not be in the usual water samples. Measurements with radium-226 tracer were performed in parallel to determine the extent of interference and the possibility of simultaneous measurements in some instances.

Additional work is planned to understand the decreased barium sulfate yield at larger volumes and in tap water, and to devise conditions for maintaining higher yields. The use of mixed barium sulfate - iron hydroxide precipitate will be tested further, and other coprecipitates will be considered. Tracer studies will be performed with the mixed precipitate and with radium-228 from which radium-224 has been removed.

This set of studies should provide the framework for determining whether the three selected procedures provide acceptable screening methods for radium-228. Subsequent tests will be needed to determine the effects of various interferences and measurement parameters such as the time period between precipitation and measurement.

Table 1

Barium Sulfate Yield as Function of Water Volume

<u>Sample</u>	<u>No.</u>	<u>Volume, l</u>	<u>Yield, % \pm 1SD</u>
Deionized water	16	0.5	94 \pm 2
	6	1.0	95 \pm 1
	12	3.0	83 \pm 3
Tap water	5	3.0	73 \pm 4

Table 2
Counting Characteristics of Ra-228 and Ra-226
in Ge(Li), Proportional, and LS Detectors

<u>Detector</u>	<u>Radionuclide</u>	<u>Radiation</u>	<u>Background count rate, c/min</u>	<u>Net count rate, c/min per pCi</u>	<u>2SD⁺⁺⁺</u>
Ge(Li) gamma-ray spectrometer	Ra-228	911 keV Ac-228 gamma 338	0.05	0.019	0.05
			0.05	0.021	0.05
	Ra-226	186 keV Ra-226 gamma	0.33	0.013	0.12
Proportional counter	Ra-228	beta alpha	1.1	2.6 [*]	0.38
			0.1	1.6 [*]	0.26
7	Ra-226	beta alpha	1.1	0.73 ^{**}	0.27
			0.1	0.60 ^{**}	0.17
LS counter	Ra-228	all (channel 0-10)	77.	8.0 ⁺	1.8
	Ra-226	all (channel 0-10)	77.	4.4 ⁺⁺	1.8

* 13 - 27 hours after separation

** 20 - 21 hours after separation

+ 5 hours after separation

++ 27 hours after separation

+++ 2 standard deviation value of gross c/min per pCi for 100-min. count

Appendix A

SECTION 7
RADIUM-226 IN DRINKING WATER
RADON EMANATION TECHNIQUE
METHOD 903.1

1. Scope and Application

- 1.1 This method covers the measurement of radium-226 in a drinking water sample and would be employed after the gross alpha or the gross radium alpha screening technique had indicated possible non-compliance with the alpha radioactivity limits set forth in the Safe Drinking Water Act, PL 93-523. 40 FR 34324.
- 1.2 This method is specific for radium-226, and is based on the emanation and scintillation counting of radon-222, a daughter product of radium-226.
- 1.3 The detection limit for this method assures measuring radium-226 concentrations as low as 0.1 pCi/l.

2. Summary of Method

- 2.1 The radium-226 in the drinking water sample is concentrated and separated by coprecipitation on barium sulfate. The precipitate is dissolved in EDTA reagent, placed in a sealed bubbler and stored for ingrowth of radon-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived radon-222 daughters are in equilibrium with the parent (~4h), the scintillation cell is counted for alpha activity.
- 2.2 The absolute measurement of radium-226 is effected by calibrating the scintillation cell system with a standard solution of this nuclide.

3. Sample Handling and Preservation (see Sec. 3, Method 900.0).

4. Interferences

- 4.1 There are no radioactive interferences in this method.

5. Apparatus - See Appendix D for details and specifications.

- 5.1 Scintillation cell system. (Figure 1.)

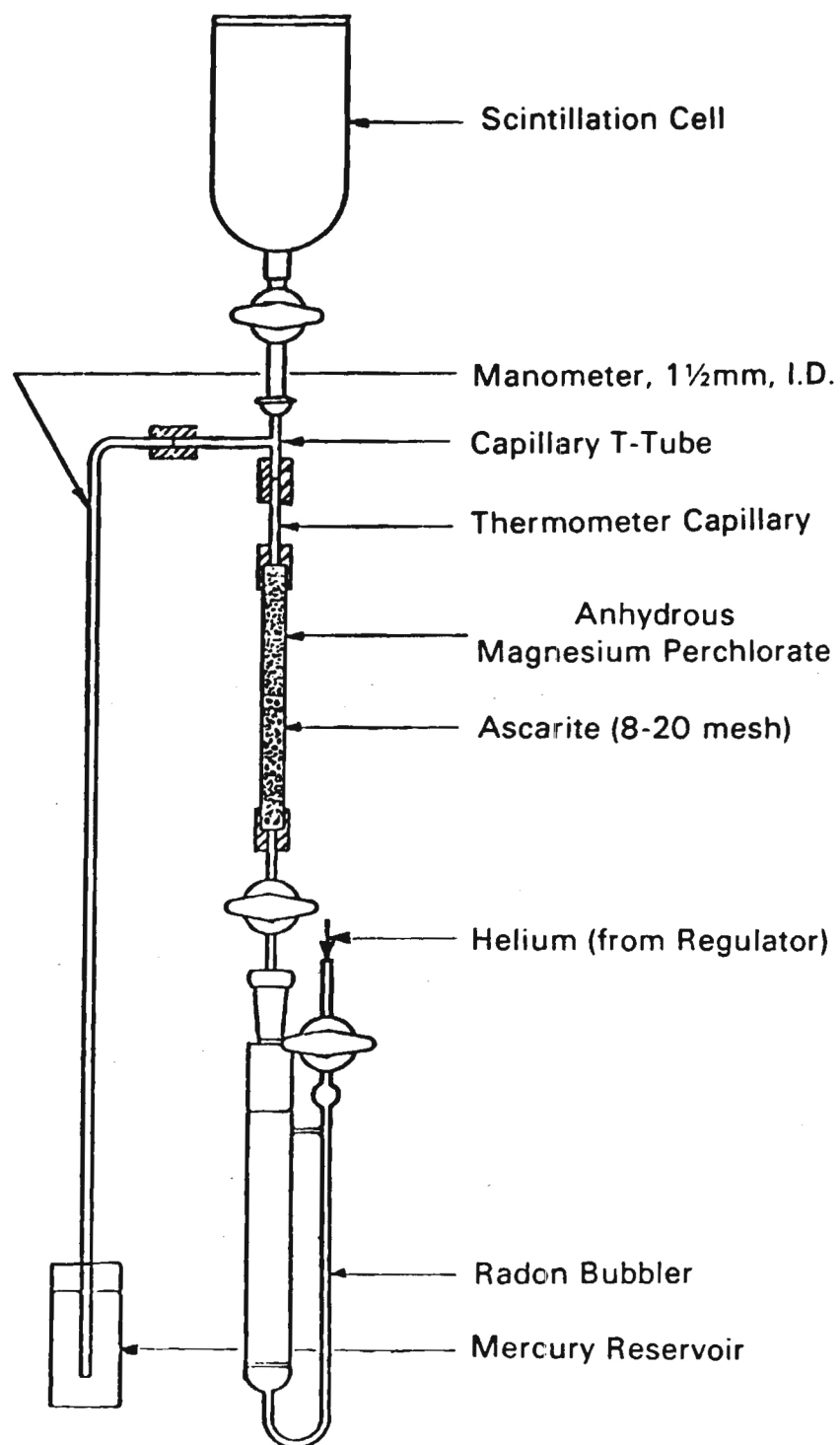


Figure 1. Radon emanation apparatus with scintillation cell

5.2 Radon emanation apparatus:

- a) Radon bubbler - (Figure 2.)
- b) Scintillation cell - (Figure 3.)

5.3 Electric hot plate

5.4 Analytical balance

5.5 Centrifuge

5.6 Glassware

6. Reagents

6.1 Distilled or deionized water.

6.2 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. gr. 0.90, 56.6%.

6.3 Ascarite, drying reagent: 8-20 mesh.

6.4 Barium carrier, 16 mg/ml, standardized: (see Sec. 6, Method 903.0).

6.5 EDTA reagent, basic, (0.25M): Dissolve 20g NaOH in 750 ml water, heat and slowly add 93g disodium ethylenedinitriloacetate dihydrate, ($\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$) while stirring. After the salt is in solution, filter through coarse filter paper and dilute to 1 liter.

6.6 Helium, gas.

6.7 Hydrochloric acid, 12N: HCl (conc.), sp. gr. 1.19, 37.2%.

6.8 Magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2$: reagent grade.

6.9 Sodium hydroxide, 10N: Dissolve 40g NaOH in 50 ml water and dilute to 100 ml.

6.10 Standard radium-226 tracer solution: preferably purchased from National Bureau of Standards, Special Publication 260, 1978, SRM 4960. Prepare stock dilution equivalent to 50 pCi radium-226 per ml.

6.11 Sulfuric acid, 18N: Carefully mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of water.

6.12 Sulfuric acid, 0.1N: Mix 1 volume 18N H_2SO_4 with 179 volumes of water.

7. Calibrations

7.1 The calibration constant of each scintillation cell must be

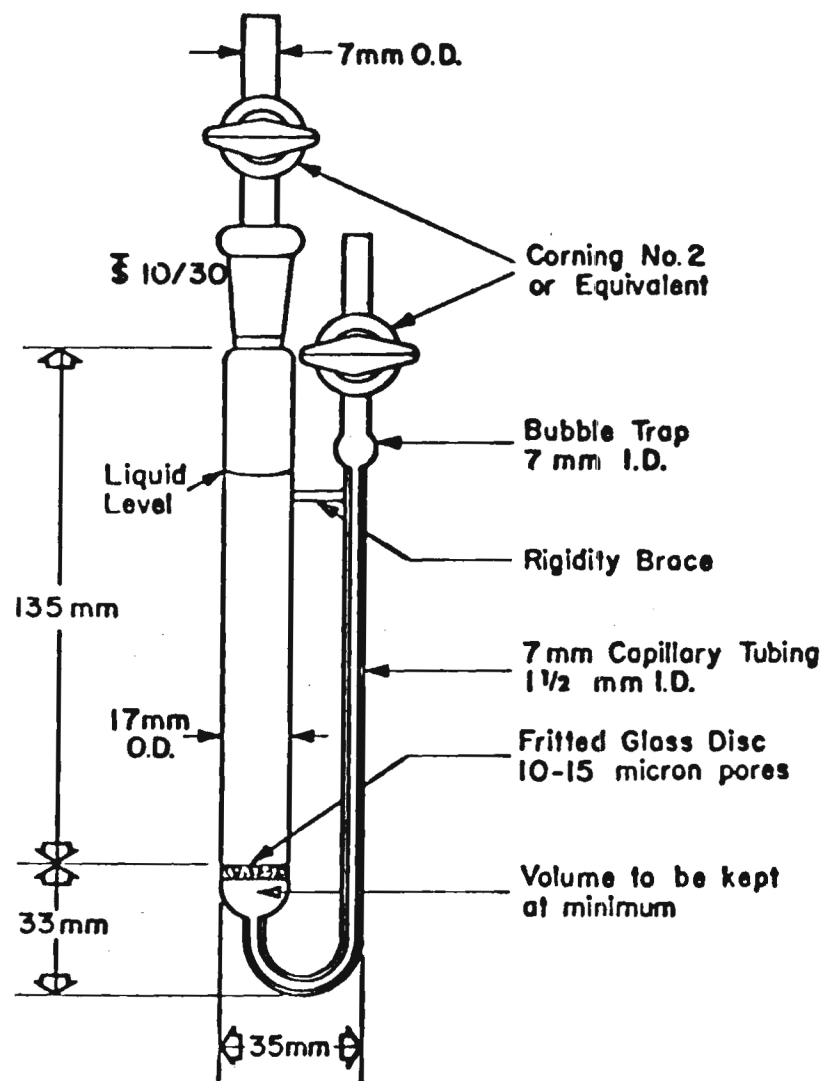


Figure 2. A typical radon bubbler

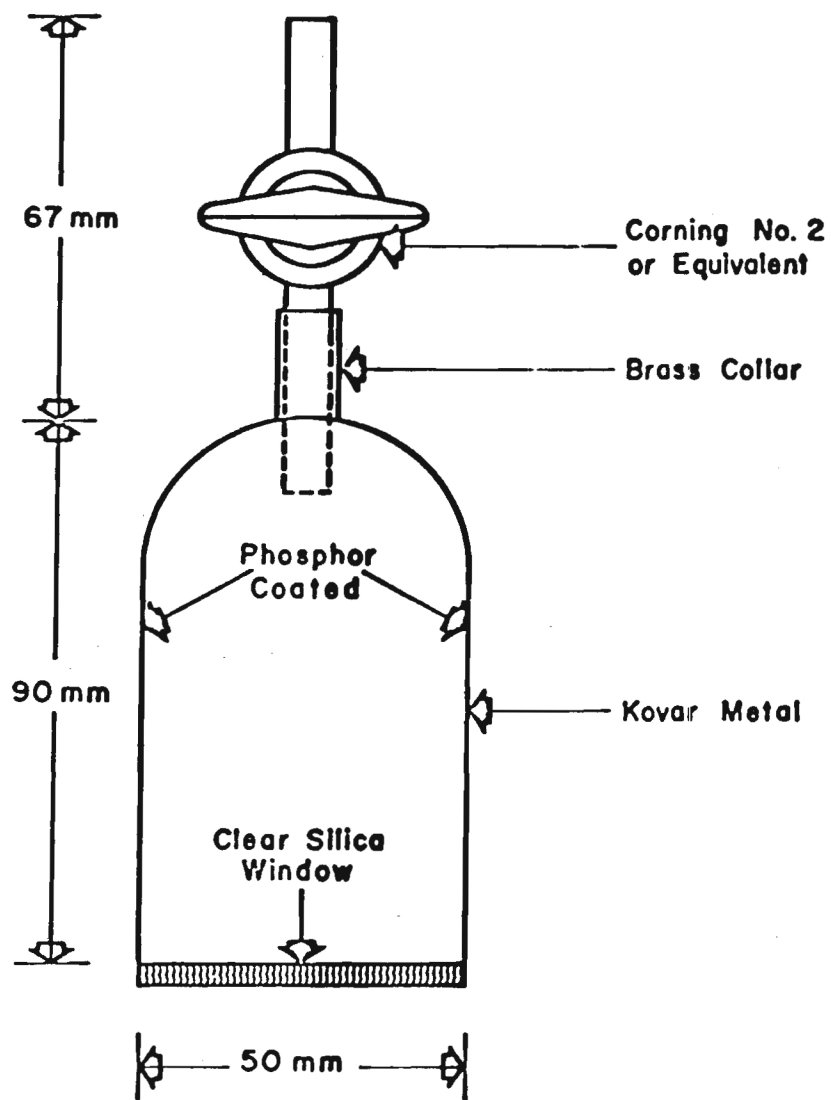


Figure 3. A typical scintillation cell for radon counting

determined using a standardized radium-226 solution with a labeled cell and a specific photon counter. This is determined as follows:

- 7.1.1 Place 50 pCi of the radium-226 standard solution in a bubbler (50 pCi of radium-226 will produce about 6 pCi radon-222 in 18 hours). Attach the bubbler to the radon assembly. (Fig. 1.)
- 7.1.2 With the scintillation cell disconnected, bubble helium gas through the solution for 20 minutes to remove all radon-222.
- 7.1.3 Close both stopcocks on the bubbler to establish zero time for ingrowth of radon-222. (Refer to 9.2) Set aside for approximately 18 hours.
- 7.1.4. Evacuate the scintillation cell and attach to the column and bubbler.
- 7.1.5. Proceed with steps 8.8 - 8.13, Radon Emanation Technique.
- 7.1.6. The calibration constant is determined from the radium-226 activity in the bubbler and the ingrowth time of radon-222.
- 7.2 The calibration constant includes the de-emanation efficiency of the system, the counting efficiency of the cell, and the alpha activity contributed by polonium-218 and polonium-214, which will be in equilibrium with radon-222 when the sample is counted 4 hours after the de-emanation. A 100-minute counting time will be sufficient for the standard and will eliminate the need to correct for decay of radon-222, which occurs during counting.
- 7.3 The bubbler used for the radium-226 standardization should not be used for sample analysis. It should be set aside to be retained for future calibrations. Each scintillation cell should be calibrated periodically with the radium-226 standard to ensure instrument quality control.

8. Procedure

- 8.1 To a 1000-ml drinking water sample, add 20 ml 12N HCl and 2.0 ml barium carrier and heat to boiling.

Note: If there is solid matter in the sample, do not filter before starting analysis. Follow procedure steps through 8.4, then filter solution into a clean centrifuge tube. Add 1 ml $(\text{NH}_4)_2\text{SO}_4$ (200 mg/ml) and stir thoroughly. Add glacial (17.4N) acetic acid (CH_3COOH) until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate. Repeat step 8.4 and continue with radium analysis.

- 8.2 Cautiously and with vigorous stirring, add 20 ml 18N H_2SO_4 . Digest 5 to 10 minutes and let precipitate settle overnight. Decant and discard supernate.
- 8.3 Slurry the precipitate and transfer to a centrifuge tube with a minimum amount of 0.1N H_2SO_4 . Centrifuge and discard supernate. Wash twice with 0.1N H_2SO_4 . Centrifuge and discard washes.
- 8.4 Add 20 ml basic EDTA reagent, heat in a water bath and stir well. Add a few drops 10N NaOH if the precipitate does not readily dissolve.
- 8.5 Transfer the solution to a radon bubbler (Fig. 2). Open both the upper and lower stopcocks and de-emanate the solution by slowly passing helium gas through the bubbler for about 20 minutes.
- Note: The volume of these bubblers is usually greater than 20 ml allowing for at least a 1 cm air space between the bubbler and the stopper. In those instances where the solution volume exceeds the capacity of the bubbler, it will be necessary to continue the boiling in the water bath until the volume is reduced.
- 8.6 Close the two stopcocks, and record time. Store the solution for 4 to 8 days for ingrowth of radon-222 (Fig. 4).
- 8.7 At the end of the storage period, fill the upper half of an absorption tube with magnesium perchlorate and the lower half with ascarite.
- Note: For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing should be used whenever possible, and the drying tube volume with the ascarite and magnesium perchlorate must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each of the drying agents occupying 4 cm and being separated by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced.
- 8.8 Attach the tube to the radon bubbler and then attach the evacuated scintillation cell (Fig. 3) to the tube. Open the stopcock on the cell and check the assembly for leaks. Gradually open the outlet stopcock on the bubbler, and when the stopcock is fully open and no further significant bubbling takes place, close the stopcock.
- 8.9 Adjust the helium gas pressure so that the gas flows at slightly above atmospheric pressure.
- 8.10 Connect the hose to the bubbler inlet and gradually open the inlet stopcock using the bubbling as a guide. When the stopcock can be

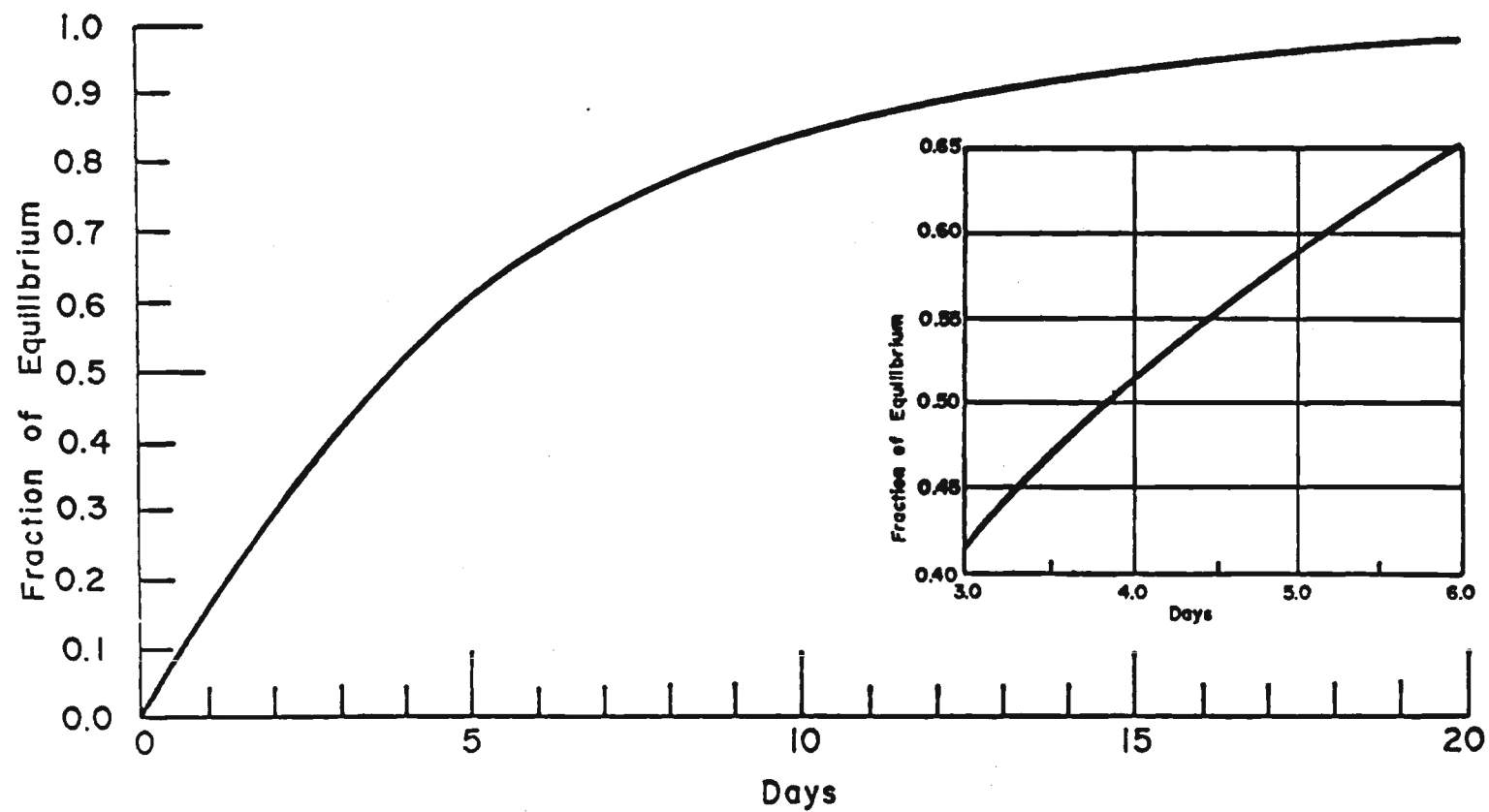


Figure 4. The growth of radon-222 from radium-226

fully opened without a significant amount of bubbling, the bubbler is essentially at atmospheric pressure again.

- 8.11 Open the outlet stopcock very slightly and allow bubbling to proceed at a rate, determined by experience, such that 15 to 20 minutes are required to complete de-emanation.
- 8.12 Toward the end of the de-emanation, when the vacuum is no longer effective, gradually increase the helium gas pressure. When the system is at atmospheric pressure, shut off the helium gas, disconnect the tubing from the bubbler inlet and close the inlet and outlet stopcocks of the cell and bubbler, and record time. This is the beginning of radon-222 decay and ingrowth of radon-222 daughters.
- 8.13 Store the scintillation cell for at least 4 hours to ensure equilibrium between radon and radon daughters. Count the alpha scintillations from the cell in a radon counter with a light-tight enclosure that protects the photomultiplier tube. Record the counting time to correct for the decay of radon-222.

Note: After each analysis, flush the cell three times by evacuation and filling with helium, and store filled with helium at atmospheric pressure. This procedure removes radon from the cell and prevents the build-up of radon daughter products. Before each analysis, the scintillation cell should be evacuated, filled with helium and counted to ascertain the cell background.

9. Calculations

- 9.1 Calculate the radium-226 concentration, D, in picocuries per liter as follows:

$$D = \frac{C}{2.22 \text{ EV}} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda_3 t_3}{1-e^{-\lambda t_3}}$$

where:

- C = net count rate, cpm,
E = calibration constant for the de-emanation system and the scintillation cell in counts per minute/disintegrations per minute of radon-222, (see 9.2),
V = liters of sample used,
t₁ = the elapsed time in days between the first and second de-emanations (steps 8.6 and 8.12) and λ is the decay constant of radon-222 (0.181 d⁻¹),
t₂ = the time interval in hours between the second de-emanation and counting and λ is the decay constant of radon-222 (0.00755 hr⁻¹),

- t_3 = the counting time in minutes and λ is the decay constant of radon-222 ($1.26 \times 10^{-4} \text{ min}^{-1}$), and
 2.22 = conversion factor from dpm/pCi.

9.2 The calibration constant, E, is determined by the following equation:

$$E = \frac{C}{A (1 - e^{-\lambda t_1}) (e^{-\lambda t_2})}$$

where:

- C = net count rate, cpm,
 A = activity of radium-226 in the bubbler (dpm),
 t_1 = ingrowth time of radon-222 in hours,
 t_2 = decay time of radon-222 in hours occurring between de-emanation and counting, and
 λ = decay constant of radon-222, ($0.00755 \text{ hour}^{-1}$).

10. Precision and Accuracy

A number of laboratories which participate in the EPA, EMSL-Las Vegas intercomparison program for radium-226 in water used this method in their analyses of water samples received in that program for the period 4/78 through 12/78. Five intercomparison studies for radium-226 in water were conducted during that period. Two of the five studies were "Performance Studies" in which the sample contained other radionuclides. In the other three studies the samples contained only radium-226, radium-228 and their decay products. The radium-226 concentrations in the test samples for the five studies ranged from 3.7 to 9.2 pCi/l, all low level, which should relate well to drinking water supplies. Data from those five studies were used for this precision and accuracy evaluation of the method.

- 10.1 The number of laboratories that participated in the five studies (labs that were called and indicated that they used this method) ranged from 12 to 17 laboratories per study. The results from one laboratory in one study was rejected as an "outlier" as determined by the T test (ASTM Standards, Part 31, page 15, 1978). All laboratories reported triplicate analyses for each study (one test sample per study). The total number of analyses for the five studies was 207 of which 174 were acceptable results (within 3 sigma of the known value, 1 sigma being 15% of the known value). This calculates to be 84% acceptability of results as determined by this method.
- 10.2 A statistical evaluation of the data from the five studies was made according to the methods of Youden⁽⁴⁾ and Steiner⁽⁵⁾. The coefficient of variation for within-laboratory error ranged from 6.4% to 19% with an average of 10.2% for the five studies. The coefficient of variation for systematic error between laboratories ranged from 14% to 18% with an average of 16.2% for the five studies. The coefficient of variation for the total error between laboratories based on a single analysis ranged from 16% to 26% with

an average of 19.4% for the five studies. A comparison of the grand average values with the known values in a test for systematic error in a method gave a value for one of the studies higher than the critical value, indicating a bias (low) for the method. However, values for the other four studies were well below the critical values, indicating no bias for the method.

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Appendix B

DETERMINATION OF GROSS ALPHA ACTIVITY IN DRINKING WATER BY COPRECIPITATION

1. Scope and Application

- 1.1 Many drinking water supplies contain dissolved solids at such high concentrations (>500 mg/liter) that measurement of gross alpha activity, by evaporating an aliquot of a sample and counting for alpha activity, seriously lacks sensitivity and reproducibility. The nitrated salts (formed by evaporation of sample aliquot containing nitric acid) of some water samples are hygroscopic and must be converted to the oxides by heating to get a stable sample residue.
- 1.2 This method provides for the separation of all actinide alpha emitting radionuclides by coprecipitation with barium sulfate and iron hydroxide from liter samples of drinking water. Dissolved solids problems are eliminated. Sensitivity can be increased by using larger sample aliquots. Reproducibility is improved by the use of constant amounts of carrier (barium and iron).
- 1.3 This method provides for a screening measurement to indicate whether specific radium-226 and/or uranium analysis is required for a drinking water supply.

2. Summary of Method

- 2.1 An aliquot of a drinking water sample is acidified with sulfuric acid and boiled vigorously for 10 minutes to outgas carbon dioxide and radon-222 from the sample. Barium carrier is added and the aliquot is stirred for about 30 minutes to coprecipitate radium with barium sulfate.
- 2.2 Iron carrier is then added to the aliquot, then is neutralized with ammonium hydroxide and is continued to be heated and stirred for another 30 minutes to coprecipitate other alpha emitters with iron hydroxide carrier.
- 2.3 The coprecipitate is filtered, dried and counted for alpha activity.

3. Sample Handling and Preservation

- 3.1 A representative sample must be collected from a free flowing source of drinking water, and should be large enough so that meaningful aliquots can be taken. Contamination from the collection system should be avoided by assuring that no contact occurs between the tap and the mouth of the container.

- 3.2 To minimize adsorption losses to the walls of the sample container, it is recommended that samples be preserved at the time of collection by the addition of 5 ml of 70 percent HNO_3 (concentrated) per liter of sample, making the samples 0.35% HNO_3 solutions. Samples can be acid-preserved when they arrive at the laboratory. They should then be stored (after acid addition) for at least 16 hours (overnight) before aliquots are taken for analysis.

4. Interferences

- 4.1 Since gross alpha screening of drinking water samples is primarily addressing radium concentrations (especially radium-226); and since the radium isotopes decay to short lived progeny, standards and samples should be counted at as nearly the same elapsed time as possible after alpha activity precipitation. If there are wide differences in the elapsed times for standards and samples, in the elapsed time range of 0-20 days, there will be significant errors in the counting efficiencies used. It is recommended that a short time be allowed between the alpha activity precipitation and the mid-point of the alpha count. However, 3 hours should be allowed for the decay of the radon-222 progeny before starting the alpha count.
- 4.2 Samples that contain sulfate and/or hydroxide insoluble precipitates will have greater total precipitates than from the added barium and iron carriers, and therefore will have counting efficiencies that are biased low.
- 4.3 Iron hydroxide precipitate collected on membrane filters without a holding agent will flake when dried and easily separate from the filter. Five (5) mg of paper pulp fiber added to the sample will greatly help to secure the iron hydroxide to the filter. Glass fiber filters are recommended over membrane filters because the surface glass fibers also help to secure the precipitate to the filter.

5. Apparatus

- 5.1 Hotplate/magnetic stirrer and stirring bars.
- 5.2 Glassware.
- 5.3 Filter membranes, 47 mm dia., 0.45 micrometer pore size or glass fiber filters, such as Gelman Type A/E or Millipore Type AP.
- 5.4 Drying lamp.
- 5.5 Planchets, stainless steel, 2 inch diameter.
- 5.6 Alpha scintillation counter or low background proportional alpha counter.

6. Reagents

- 6.1 Ammonium hydroxide, 6M. Dilute 400 ml reagent grade NH_4OH to 1 liter with distilled water.
- 6.2 Barium carrier, 5 mg Ba^{+2} /ml. Dissolve 4.4 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 500 ml *4.40g* distilled water.
- 6.3 Bromocresol purple, 0.1 percent. Dissolve 100 mg of the water soluble reagent in 100 ml distilled water.
- 6.4 Iron carrier, 5 mg Fe^{+3} /ml. Dissolve 17.5 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 200 ml distilled water containing 2 ml 16M HNO_3 . Dilute to 500 ml.
- 6.5 Sulfuric acid, 1M. Dilute 55 ml of the 96 percent reagent grade H_2SO_4 to 1 liter with distilled water.
- 6.6 Paper pulp/water mixture - add a 0.5 g paper pulp pellet to 500 ml of distilled water plus 5 drops of a (1+4) detergent plus water solution in a plastic bottle. Cap the bottle and stir vigorously for 3 hours before using. This mixture should be stirring when an aliquot is taken.
- 6.7 Five drops of a (1+4) detergent plus water solution added to the sample will prevent the precipitate from collecting on the beaker wall and will assist in filtering the precipitate. (Examples of wetting agents: Rohm and Haas Triton N101 or Triton X100.)

7. Calibration

- 7.1 Thorium-230 is a recommended pure alpha emitter for gross alpha efficiency calibration especially if the alpha contribution to the beta channel is to be determined. If only gross alpha measurements are to be made on samples, natural uranium is an adequate standard for gross alpha counting efficiency calibration.
- 7.2 Spike 500 ml portions of tap water in separate beakers (at least 3) with known amounts (at least 100 pCi) of standard alpha emitter activity. Add 2.5 ml of HNO_3 (Conc.) to each spiked sample. With these spiked samples, determine a counting efficiency (cpm/pCi) for the alpha emitter by taking the samples through the procedure (parts 8.1 - 8.10).
- 7.3 Unspiked tap water portions (500 ml) should be taken through the procedure for blank corrections of alpha activity in the tap water plus the reagents used.
- 7.4 Calculations

$$\text{Efficiency, cpm/pCi} = \frac{\bar{C}_s - \bar{C}_b}{\text{pCi}}$$

\bar{C}_s = mean spiked sample counts per minute
 \bar{C}_b = mean blank counts per minute
 pCi = spike activity

8. Procedure (The following method was presented by Robert Lieberman of the Eastern Environmental Radiation Facility, Montgomery, Alabama, at the Health Physics Society meeting in Las Vegas, Nevada, August 1982. Some minor changes were made as a result of a single laboratory test of the method by the EMSL-Las Vegas, Quality Assurance Division.)
- 8.1 Use a measured aliquot of water sample. If the sample is less than 500 ml, dilute to 500 ml with distilled water. Samples of 500 ml to 1 liter use as is.
- 8.2 Add 5 drops of the (1+4) detergent plus water reagent.
- 8.3 Place the sample on a magnetic stirrer/hot plate and, while stirring, gently add 20 ml of 1M H_2SO_4 and boil for 10 minutes to flush carbon dioxide (from carbonates and bicarbonates) from the sample. Radon will also be flushed from the sample.
- 8.4 Lower the hot plate temperature to below sample boiling, continue stirring and add 1 ml of barium carrier solution (5 mg Ba/ml). Continue stirring for 30 minutes.
- 8.5 Add 1 ml of bromcresol purple indicator solution, 1 ml of iron carrier solution, and 5 ml of paper pulp/water reagent (aliquot taken while the paper pulp/water mixture is stirring).
- 8.6 Continue stirring and add 6M NH_4OH dropwise to the sample until there is a distinct color change (yellow to purple). Continue warming and stirring for 30 minutes.
- 8.7 Filter the sample through a glass fiber filter (or membrane filter if further analysis is to be done), rinsing all precipitate from the beaker to the filter. Wash the precipitate with 25 ml of distilled water.
- 8.8 Allow 3 hours for the collected radon progeny to decay and to dry the filter at 105°C or under a mild heat lamp.
- 8.9 Count the filters for gross alpha activity. An early count of the gross alpha activity, after the 3 hour decay period, is recommended to minimize additional radon ingrowth which is not easily corrected for when there are other alpha emitters in the sample.
- 8.10 Store samples in a desiccator if they are to be recounted at a later date.

8.11 Prepare a reagent blank precipitate to determine the reagent alpha activity background.

9. Calculations

$$9.1 \text{ Gross alpha activity, pCi/liter} = \frac{C_1 - C_B}{E V}$$

E = counter efficiency, cpm/pCi
V = volume analyzed, liters.
C₁ = sample, counts per minute.
C_B = reagent blank, counts per minute.

9.2 Lower Limit of Detection, LLD

$$\text{LLD, Gross alpha, pCi/liter} = \frac{4.66\sqrt{C_B T}}{E V T}$$

C_B = reagent background, counts per minute.
T = counting time.
E = counter efficiency, cpm/pCi
V = sample volume, liters.

This LLD calculation is valid if the sample counting time is equal to the background counting time.

10. Precision and Accuracy

(To be added from single laboratory and multilab tests of the method.)

Appendix A

Total alpha factors for radium-226 with change in elapsed time between alpha activity precipitation and the midpoint of the alpha count (from Kirby's tables, "Decay and Growth Tables for the Naturally Occuring Radioactive Series, AEC Research and Development Report MLM-2042).

<u>Elapsed Time</u> <u>Δt = hrs, (days)</u>	<u>Total Alpha Factor</u> <u>*</u>	<u>***</u>
0	1.0000	1.5100
4	1.0800	1.5900
8	1.1668	1.6768
12	1.2511	1.7611
16	1.3329	1.8429
20	1.4123	1.9223
24 (1)	1.4893	1.9993
36	1.7068	2.2168
48 (2)	1.9055	2.4155
60	2.0870	2.5970
72 (3)	2.2528	2.7628
84	2.4042	2.9142
96 (4)	2.5424	3.0524
(5)	2.7841	3.2941
(6)	2.9856	3.4956
(8)	3.2941	3.8041
(10)	3.5087	4.0187
(15)	3.8015	4.3115
(20)	3.9198	4.4298
(25)	3.9675	4.4775
(30)	3.9869	4.4969

* This data, from Kirby's tables, assumes a pure parent at $\Delta t=0$.

** This data is (*) plus a 0.51 fraction of Po-210 which is also an alpha emitter. The ratio of Po-210 to Ra-226 in the EMSL-LV Ra-226 standard (March 23, 1984) is 0.51.



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June 2, 1988

Dr. Chung King Liu
Nuclear Radiation Assessment Division
EMSL/US EPA
P.O. Box 15027
Las Vegas, NV 89114

Dear Dr. Liu:

The sixth quarterly report of the project "Screening Method for Radium-228 in Drinking Water" is enclosed for your information and evaluation. Please let me have any suggestions or comments that you consider appropriate.

Sincerely yours,

Bernd Kahn

BK/rs

Enclosure

Screening Method for Radium-228 in Drinking Water

Report for Sixth Quarter
January 10, 1988 - April 10, 1988

Introduction

Counting efficiencies for the characteristic gamma rays emitted by daughters of Ra-228 and Ra-226 were confirmed for the Ge(Li) detector used in this study to permit calculations of radium levels and detection limits in samples. Measurements of EPA Intercomparison Study samples was begun to test the method, but is being interrupted to determine the cause of some low barium sulfate chemical yields in these samples. Measurements of blanks has also been begun, and the cause for some detectable Ra-226 in these samples is being examined. Measurements of Ra-228 in dissolved barium sulfate liquid were performed, by liquid scintillation counter using both a conventional scintillator in organic solvent and pure water samples. The latter were measured by detecting Cherenkov radiation from energetic Ac-228 beta particles.

Counting Sensitivity for Ra-228 and Ra-226 Tracers

The sensitivity of counting Ra-228 and Ra-226 daughters with a Ge(Li) detector was checked by determining detector counting efficiencies and using previously measured radiation background values. The samples consisted of 86 pCi Ra-228 and 95 pCi Ra-226, separately precipitated and collected on Gelman type A/B filters over an area of 12 cm² (39 mm dia.). The chemical yield was 96 and 98 percent for Ra-228 and 100 percent for Ra-226 duplicate samples. The samples were counted for 50,000 seconds each, with the counting efficiencies listed in Table 1. The counting efficiencies of these and other gamma rays from the radioactive daughters of Ra-228 and Ra-226 are consistent with each other and gamma rays from other radionuclides in yielding a straight line on a log-log graph between about 200 and 2,000 kev, except for the low efficiency for the 609-kev peak. The latter is attributed to extensive coincidences with other gamma rays from Bi-214 at this relatively high counting efficiency. The listed gamma-ray fractions and counting efficiencies give the following multiplication factors from net counts per 6,000 seconds to pCi:

Ra-228	338 kev	0.60
	911	0.68
Ra-226	352	0.20
	609	0.32

The gamma-ray backgrounds listed in Table 1 are the averages of six consecutive week-end measurements obtained for 200,000-second periods, given in previous quarterly reports. The peaks are net count rates due to the natural radiation background recorded by the detector within a 10-cm lead plus 1-cm steel shield. Part may be due

to background in the detector and associated parts within the shield, and part may be due to radiation entering through the unshielded section where the detector is connected to the dewar flask, or radon daughters within the shielded volume. The continuum background is calculated from the average count rate in four channels -- two on each side of the peak -- by multiplying this sum by the ratio of the number of channels under the peak to the four channels. Typical number of channels under the peaks in the background measurements are 3 - 6. The number of channels under the peak increases with the size of the peak, but is not much greater than for the background in the range of 0-5 pCi/liter. The uncertainty values listed in Table 1 are the standard deviations for six replicate measurements. These exceed the statistical standard deviation of counting, presumably because of the variation in radon levels in counting room air.

The detection limits at 1 and 5 pCi/liter, defined as the 1.96-standard deviation value of the net count rate of the sample according to Section 141.25(c)(2) of the NIPDW Regulations, are calculated in Table 2. The net count rates are calculated from the above-listed multiplication factors for samples of 1 gallon (3.785 liters) for which the radium is recovered with 92 percent yield and the radioactive daughters reach 100 percent equilibrium. The gross counts are the sums of the net counts and the two backgrounds for each gamma ray. The 1.96-standard deviation values for the gross counts are listed in Table 2, both for each gamma ray measured separately and for the combined results, i.e., for the radionuclide concentration obtained by averaging the results from the two gamma rays.

The results in Table 2 predict a detection limit of 1 pCi/liter at a concentration of 1 pCi/liter for both Ra-228 and Ra-226. at the maximum contaminant level of 5 pCi/liter, the 2-standard deviation value is 2 pCi/liter for Ra-228 and 1 pCi/liter for Ra-226, separately, and would not exceed 2 pCi/liter for any combination of the two radionuclides at 5 pCi/liter. These uncertainties are similar to the ones for the gross alpha particle activity screening procedure. The detector efficiency, which is one of the factors controlling the detection limit and standard deviation, is believed to be typical of such detectors purchased during the past five years. Larger detectors available today have nominal Co-60 counting efficiencies of about 40 percent, which might lower these values by about 30 percent. Some laboratories may use small detectors with efficiencies that are lower by as much as 40 percent, which would increase detection limits and standard deviations in proportion. In that case, it will be necessary to increase data collection by including the 968 kev gamma ray (16.2%) of Ac-228, to lengthen the counting period.

The calculated results are consistent with measured Ra-228 values for a sample of 4.2 pCi which was counted eight times. The average value was 5.0 pCi and the 2-standard deviation value was 5.1 pCi (see report for fourth quarter), for a value of 1.3 ± 1.3 pCi/liter per gallon sample.

Radium Levels in Blank Samples

Triplicate samples of deionized water were analyzed to check for potential contamination of Ra-228 or Ra-226 in the procedure. The results, in Table 3, show no significant amounts of Ra-228, but do show some Ra-226. The average concentration of Ra-228 is 0.5 ± 0.1 pCi/liter but the typical standard deviation due to counting is 1.1 pCi/liter. The average concentration of Ra-226 is 2.0 ± 1.0 pCi/liter, and the standard deviation due to counting is 0.9 pCi/liter. The elevated level of Ra-226 could be in the planchet, the filter paper, the barium sulfate or the water.

Precipitation Yield for Radium Sulfate

In testing the procedure with six USEPA Intercomparison Study aliquots, the average chemical yield was below the typical yield obtained with local tap or demineralized water. The yields were as follows:

93.3 %
91.2
86.8
86.5
58.3
44.7

The expected weight of barium sulfate was 86 mg. In view of the four yields below 90 percent, and particularly the very low yields for the fifth and sixth samples listed above, additional studies were performed.

The obvious difference in the Intercomparison Study solution is the acid strength of 0.5 M HCl. The other test samples contain 1 ml concentrated nitric acid per liter for initial sample preservation and 20 ml concentrated hydrochloric acid per liter to maintain radionuclides that have soluble sulfates in solution, yielding an acid strength of 0.25 M. However, further studies with precipitating barium sulfate at both acidities from tap water and Intercomparison Study samples showed no consistent behavior with regard to yields.

Radium-228 Measurements with Liquid Scintillation Detector

Two samples of Ra-228, each of 864 pCi, were purified by the recommended EPA procedure for Ra-228 and the final barium sulfate precipitate was dissolved with 10 ml 0.25 M EDTA. One sample was mixed with 10 ml of a conventional LS cocktail; the second sample was diluted with water to 20 ml. Both samples were placed in a LS vial and, after 36 hours to await ingrowth of Ac-228, were counted in a LS counter, obtaining a sample spectrum with the 3-channel system.

The first sample had a counting efficiency of 102 percent relative to Ra-228, resulting from counting both Ra-228 and Ac-228 beta particles. Of the activity, 20 percent is between channel 0 and 2.5, and indicates low energy beta particles (below 100 kev),

presumable due to Ra-228. The remaining 82 percent are energetic beta particles in channels 2.5 to 7.5.

The second sample, without scintillator, was used to count Cherenkov radiation in the LS detector. It had a counting efficiency of 11.8 percent, and all counts were in channels 0 to 3.5. Presumably, the more energetic beta particles emitted by Ac-228 were counted by this interaction.

The total background for liquid scintillation counting was 70 counts/minute, of which 27 counts/minute were in channels 0 - 2.5, and 43 in channels 2.5 - 7.5. Hence, the minimum detectable level at the indicated counting efficiency for a 100-minute counting period is 1.1 pCi, either for the entire energy range or for channels 2.5-2.7, or 0.3 pCi/liter for a 3.8-liter sample. For Cherenkov counting, the background was 30 counts/minute. The minimum detectable level for a 100-minute counting period is 6.3 pCi, or 1.7 pCi/liter for a 3.8-liter sample.

Summary and Discussion of Future Work

The calculations and measurements for the gamma-ray spectral analysis of Ra-228 and Ra-226 show that both radionuclides may be measured with sufficiently low detection limits when a 1-gallon sample is processed by barium sulfate precipitation and counted on a conventional Ge(Li) or GeHP detector with nominal Co-60 counting efficiency near 25 percent. During next quarter, variations in the chemical yield of barium sulfate will be examined to assure that the recommended procedure consistently provides yields above 90 percent; possible sources of Ra-226 contamination will be considered to assure that blank samples are as close to zero radium content as possible; and tests with Intercomparison Study solutions will be continued.

Tests with a liquid scintillation counter indicate that the counting efficiency for Ac-228 is sufficiently high and the background is sufficiently low that the intended detection limit of 1 pCi/liter will be reached with a 1-liter sample counted for 100 minutes or a 50-minute counting period for a gallon sample. The Ac-228 beta particles that constitute the major source of count rate, however, may not be readily distinguishable from other radionuclides carried on the barium sulfate precipitate with the simple 3-channel detectors that are commonly available. This will have to be checked.

Table 1

Detector Characteristics for Counting Ra-228 and Ra-226

<u>Isotope</u>	<u>Gamma-ray energy, keV</u>	<u>Gamma-ray fraction, %</u>	<u>Peak detection efficiency, %</u>	<u>Background, count/6000s</u>	
				<u>continuum</u>	<u>peak</u>
Ac-228	338.4	11.3 \pm 0.3	6.6	15 \pm 3	3 \pm 1
Ac-228	911.1	26.6 \pm 0.7	2.5	6 \pm 1	3 \pm 1
Pb-214	351.9	35.4 \pm 0.3	6.4	18 \pm 4	17 \pm 6
Bi-214	609.3	44.8 \pm 0.4	3.1	13 \pm 2	14 \pm 5

Notes:

1. The gamma-ray fraction information is as of April 1984, from NCRP Report No. 58, pp. 493-500.
2. The counting efficiency and background are for a cylindrical Ge(Li) detector, 59.5 mm long, 53 mm dia., open end, P-core, nominal Co-60 efficiency 24.6%.
3. The background continuum is the average count rate per channel at both sides of the peak, multiplied by the number of channels in the peak; the background peak is measured in the absence of a sample. Both values were measured for 200,000-s periods.
4. The peak detection efficiency for the 6093 keV Bi-214 peak is 20% lower than expected because of gamma-gamma coincidences when the 47-dia. filter is counted in a steel planchet directly on the surface of the detector.

Table 2

Calculated Standard Deviation of Measuring 3.78 Liter Samples
at Radium Concentrations of 1 and 5 pCi/l

Gamma-ray energy, keV	net counts/6.000s		gross counts/6,000s		s.d./6,000s		2.s.d, pCi/l	
	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi

Radium-228 at equilibrium

338.8	5.8	28.9	24	47	5.8	7.5	2.0	2.6
911.1	5.1	25.7	14	35	4.0	6.1	1.6	2.4
combined	—	—	—	—	—	—	1.2	1.7

Radium-226 at equilibrium

351.9	17.6	87.9	53	123	10.2	13.2	1.2	1.5
609.3	10.8	53.9	38	81	8.2	10.4	1.5	1.9
combined	—	—	—	—	—	—	1.0	1.2

- Notes:
1. net counts = $\text{pCi} + 6,000 \times 0.037 \times 0.92 \times e \times f$
where e = counting efficiency, f = gamma fraction, and 0.92 is average chemical recovery.
 2. gross counts = net counts plus background continuum and peak.
 3. standard deviation (s.d.) per 6,000-second count = $(\text{gross count} + \text{s.d. (continuum)}^2 + \text{s.d. (peak)}^2)^{0.5}$.
 4. 2 s.d. value in pCi/l = $2 \times \text{s.d. per 6,000 s}$ ($6,000 \times 0.037 \times 0.92 \times 3.78 \text{ ef}$).
 5. The s.d. for measuring one of the radium isotopes with two gamma rays is: $(\text{s.d.})^2_{\text{combined}} = 0.5 (\text{s.d.})_1^2 + 0.5 (\text{s.d.})_2^2$

Table 3

Radium Analysis of Blank Water Samples

<u>Ra-228</u>	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
338-keV, counts/6,000s	4.5±12	6.5±10	3.7±10
911-keV	1.2±6.6	0.6±7.3	3.1±8.7
338-keV, pCi/gallon	2.6±7.0	4.0±6.2	2.2±6.0
911-keV	0.8±4.4	0.4±5.1	2.2±6.2
both	1.7±4.1	2.2±4.0	2.2±4.3
average, pCi/liter	0.5±1.1 (±0.1)		
<u>Ra-226</u>			
352-keV, counts/6,000s	26±18	32±19	24±19
609-keV	3.1±13	41±19	41±18
352-keV, pCi/gallon	5.6±3.8	6.4±3.9	5.0±3.9
609-keV	1.1±4.6	13.5±6.2	13.7±6.2
both	3.4±3.0	10.0±3.7	9.3±3.7
average, pCi/liter	2.0±0.9 (±1.0)		
chemical yield, %	90.9	95.7	94.3

Note: Plus/minus values are 1 standard deviation of counting; for the average values, the first plus/minus value is the average standard deviation for the three measurements, while the value in parentheses is the value calculated from the three measurements.

E-25-m16



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December 9, 1988

Dr. Chung King Liu
Nuclear Radiation Assessment
EMSL/US EPA
P.O. Box 15027
Las Vegas, NV 89114

Dear Dr. Liu:

The draft report, "Screening Method for Radium-228 in Drinking Water," is enclosed for your review and comments. I will be glad to discuss this with you and make corrections as appropriate. I am sorry that we had to request a 2-month delay. As you can see, there is still one item that needs to be resolved in the study, but that can be done later.

Thank you.

Sincerely yours,

A handwritten signature in cursive script that reads "Bernd Kahn".

Bernd Kahn

BK/rs

Encl.

cc: Pete Dawkins (OCA)

Draft Final Technical Report
Screening Method for Radium-228 in Drinking Water

Bernd Kahn, Principal Investigator
Nuclear Engineering and Health Physics Program
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Project period: Oct 1986 - Oct 1988

Draft report: December 1988

Prepared for the

US Environmental Protection Agency

Assistance ID No. CR-813-630-01

ABSTRACT

Methods for measuring radium-228 were reviewed to select a brief and simple screening procedure under NIPDW Regulations for public water supplies. A two step method was considered, by which the sample is concentrated by evaporation or precipitation, and then counted with a proportional (or Geiger-Mueller) detector, a liquid scintillation detector, or a germanium detector with multichannel analyzer.

Gross beta particle counting was found to be a feasible option for meeting the 1 pCi/L detection limit, utilizing current sample volumes, and processing samples with commonly available equipment in reasonable time periods. Appropriate sample volumes and counting periods were estimated on the basis of known counting efficiencies and background count rates.

Gamma-spectral analysis is the recommended option because radium-226 and radium-228 can be determined directly and simultaneously. Several aspects of the method were tested to assure that the concentration procedure is near-quantitative and that the detection limit can be reached with a 3.8-L sample and a 6,000-s counting period. The method was tested with radium tracer solutions, EPA intercomparison samples, water supply samples, and blanks. The method was shown to be appropriate for radium-228 analysis over the range of 1 to 25 pCi/L; additional work is needed for radium-226 analysis to examine the cause of some elevated results.

INTRODUCTION

More than 50,000 community water systems in the U.S. are monitored in 4-year cycles to determine whether the combined content of radium-226 and radium-228 exceeds the maximum contaminant level (MCL) of 5 picocuries per liter (pCi/L). Because radium analyses are relatively labor intensive, the National Interim Primary Drinking Water (NIPDW) Regulations provide a screening procedure according to which radium-226 must be measured only if the gross alpha particle activity exceeds 5 pCi/L. Radium-228 must then be measured if radium-226 exceeds 3 pCi/L (US EPA 1976). Gross alpha particle activity screening measures the alpha particles emitted by radium-226, while screening for radium-228 was justified by the belief that only rarely would the concentration of radium-228 exceed that of radium-226 (US EPA 1976). Data subsequently obtained during the nationwide monitoring program has invalidated this belief (Blanchard et al. 1985), and stimulated the present search for an alternative measurement procedure for radium-228 in water, either by screening or with a brief and simple analytical method.

The prescribed procedure for radium-228 analysis (Krieger and Whittaker 1980) under the NIPDW Regulations consists of precipitating radium with combined barium and lead sulfates from an acidified 1-liter sample. Interferences are removed by repeatedly precipitating the sulfates in EDTA solution and by lead sulfide scavenging. After

storage for at least 1.5 days to permit ingrowth of the 6.13-h actinium-228 daughter of 5.76-y radium-228, actinium-228 is coprecipitated from the purified solution with yttrium carrier, first as hydroxide and then as oxalate. The actinium-228 is immediately counted with a low-background gas proportional or Geiger-Mueller detector. Chemical yields for radium and actinium are determined by weighing the barium sulfate and yttrium oxalate precipitates. Another procedure provides alternatives for separation and purification by solvent extraction, and depends on reproducibly high recovery instead of measuring yields (Percival and Martin 1974).

This study surveyed available procedures for their applicability for screening or simple analysis, estimated some parameters to determine whether the four more promising approaches would meet the criteria for such use, and then validated a selected procedure. The criteria were that the analysis could be performed with the currently collected 1-gallon (3.78-L) water sample by the laboratories that currently analyze these samples, and would not exceed the detection limit of 1 pCi/L at the 95% confidence level of present procedures (US EPA 1976). A laboratory was expected to process approximately 20 samples per week plus associated blank and known samples, and to measure them with available radiation detectors.

METHODS REVIEW

Noyce (1980), in reviewing radium-228 analyses of water samples published from 1967 to 1980, described several methods that are the

precursors of the above-cited methods for successively separating radium and actinium, and then counting the actinium-228 beta particles with a gas-filled detector. Radioactive interferences in drinking water samples are mainly other uranium- and thorium-chain radionuclides. Initial concentration and purification can be by sorption on manganese-dioxide-coated filters or by precipitating ferric hydroxide and barium sulfate.

Further purifications were by repeated precipitations, solvent extraction, or ion exchange. Liquid scintillation (LS) counting, alpha particle spectrometry (for the 1.91-y thorium-228 daughter of actinium-228 which slowly grows into purified radium-228), and beta-gamma coincidence counting of actinium-228 were also used.

Methods development along these lines has continued. Brooks and Blanchard (1980) purified radium by solvent extraction after an initial barium sulfate precipitation. Krieger and Whittaker (1980) describe gross beta counting of an evaporated water sample. Lieberman (1984) precipitated mixed ferric hydroxide and barium sulfate for gross activity screening. Henry (1982) and Bivens (1986) concentrated radium by barium sulfate precipitation and determined radium by gamma-ray spectrometry. Velten (1983) converted barium sulfate first to the carbonate and then to the acetate to obtain radium soluble in an organic LS cocktail. Godoy and Schuettelkopf (1983) counted Cherenkov radiation from an aqueous solution of radium in a liquid scintillation detector. McCurdy and Mellor (1981) expanded their coincidence technique by determining actinium-228 by beta-gamma coincidences and

radium-226 by alpha-gamma coincidences.

The four approaches listed in Table 1 were selected from these procedures to consider screening for the presence of radium-228 at levels that, combined with radium-226, would exceed the MCL. Each approach consists of only two steps -- concentration and radioactivity measurement. The sample volumes and counting times required to achieve a detection limit of 1 pCi/L were estimated on the basis of counting efficiencies, background count rates, and chemical yields observed at this laboratory. The precipitate was assumed to be barium sulfate, although other concentration procedures cited above could be substituted. The elegant coincidence counting procedure was not considered because the detection system is believed to be much less commonly available than gas-filled, liquid scintillation, and germanium detectors in laboratories that perform routine radionuclide measurements.

Sample evaporation with gross beta particle counting uses the sample already prepared for gross alpha particle activity screening. The energetic beta particles of actinium-228 and possibly some weak beta particles of radium-228 are counted. In detection systems with pulse height discrimination, the beta-particle count can be obtained simultaneously with the alpha-particle count. The major limitation on the effective use of this screening approach is alpha and beta particle absorption by dissolved solids. If the dissolved solids content is below 0.3 gram/L, a 0.35 L sample can be evaporated and the counting period can be reduced to 100 minutes. On the other hand, a

dissolved solids content above 0.5 gram/L will require a smaller sample volume and counting for longer than 300 minutes.

Concentration by coprecipitation eliminates interference by dissolved solids and provides a uniform sample weight with consistent self-absorption for alpha and beta particles. Use of a 0.4-L sample permits counting with a proportional or Geiger-Mueller detector for the 100-minute period considered suitable for handling the normal sample load. Larger sample volumes would improve precision at MCL values or permit shorter measurements. The precipitate would not be expected to carry all radionuclides and thus would not provide the broad-spectrum radionuclide screening of evaporated samples. This separation is beneficial if screening is intended only for radium, but would require modifications if other radionuclides, such as uranium, were to be included in the screening.

Liquid scintillation counting after precipitation requires more sample volume because the LS detector has a higher background count rate (see Table 1). The minimum sample volume and counting period depend on the LS system, the channel width selected for optimum response, the procedure used for dissolving the solid or dispersing it in the scintillation cocktail, and the choice of cocktail (or use of Cherenkov counting in an aqueous solution). These decisions will also determine whether one counts actinium-228, radium-228 or both.

Some false positive identifications of radium-228 can be expected in all three approaches if other radionuclides that emit beta

particles are in the sample. Some interferences can be eliminated by precipitation, volatilization during evaporation, and energy discrimination. Combined alpha- and beta-particle measurements can identify some interfering radionuclides, and repeated measurements can assist by observing radioactive ingrowth or decay. Even taking this information into account, samples that could have concentrations above the MCL value will have to be analyzed for radium-226 and radium-228.

Counting by gamma-ray spectral analysis with a germanium detector can eliminate most interferences. Hence, this is a direct analytical procedure for both radium-226 and radium-228. A much larger sample volume is needed because of the relatively low counting efficiency of the detector and the low decay fractions of the characteristic gamma rays used to identify and measure these radionuclides. Because these gamma rays are emitted by radioactive progeny of the two radium isotopes, ingrowth periods after precipitation of 1.5 days and 22 days, respectively, are required before radium-228 and radium-226 can be determined from progeny that are at 98 percent of equilibrium.

In view of the possibility for direct analysis by a simple procedure, gamma ray spectrometry after concentration was selected for validation. Several variants of this approach are already in use (Michel et al. 1981, Henry 1982, Bivens, 1986,). The marginal sensitivity of the procedure, indicated by use of the entire 3.8-L sample to attain the detection limit of 1 pCi/L, is the major concern in recommending it for a nationwide monitoring concern. Studies were undertaken to check the consistency of high chemical yields for the

barium sulfate precipitation, the variability in the background due to radium daughters in the environment of the detector, and the agreement of observed with known concentrations and calculated standard deviations of measurement near the MCL.

ANALYTICAL PROCEDURES

The 3.78-liter sample is preserved by adding 4 ml concentrated (16N) nitric acid (Krieger and Whittaker 1980) or 15 ml 1 N nitric acid. To precipitate barium sulfate, the sample is further acidified with 20 ml concentrated (12 N) hydrochloric acid; 5 ml barium carrier (88 mg $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) is pipetted into the solution and mixed with it; and 20 ml 18 N sulfuric acid is added. The solution is heated to boiling while being stirred, boiled gently for 30 minutes, and then stored overnight to let the precipitate settle. The precipitate is collected on a tared glass fiber filter (Gelman type A/E, 47 mm dia.) clamped in a filter funnel. The filter is washed with 10 ml ethanol and then 10 ml diethyl ether under vacuum suction and then dried approximate 30 min. under a heat lamp. The filter with precipitate is weighed to determine the yield. At 100 percent yield, the weight of barium sulfate is 84.0 mg. An average weight loss by the filter of 0.6 mg was found when filtering 3.8 L of water.

The filter is sealed in a plastic envelope and counted on the face of a Ge(Li) detector. The detector is a right circular cylinder drifted coaxially with the closed end facing the thin aluminum window. The detector is 60 mm long and 53 mm in diameter. Its nominal

efficiency at 1.332 MeV is 24.6% relative to a NaI(Tl) detector, with a full width at half maximum of 1.9 keV. The detector and sample are in a shield of 10-cm thick lead with 20 mm copper liner except where the cryostat passes through the shield. The spectrum is collected with an 8,192-channel analyzer at 0.5 keV per channel.

Each sample is counted for 6,000 s. The count rates under two characteristic photoelectric peaks each are determined to measure radium-228 and radium-226. The background radiation due to the Compton continuum from more energetic gamma rays in the environment and the sample is determined from count rates on both sides of each peak, and subtracted from the gross count rate of the peak. In addition, the count rates of the natural radiation background peaks at these characteristic energies are determined by counting for 200,000 s every weekend, and these values are also subtracted from the gross count rates.

The activity is determined from the net count rate at each peak by dividing by the peak detection efficiency and the gamma ray fraction. Results for the two characteristic peaks are averaged.

The samples are counted after waiting for progeny ingrowth periods of at least 1.5 d in radium-228 and 22 d in radium-226. Observations of ingrowth in radium-226 showed no loss due to emanation of radon-222. Ingrowth periods for radium-226 can be reduced by calculating the fractional ingrowth of 3.82-d radon-222 and its progeny, but this change increases the detection limit.

The detection efficiency of the characteristic peaks was determined by counting barium sulfate from samples to which standard solutions of either radium-226 or radium-228 had been added. The solutions were obtained from the US EPA EMSL Las Vegas Quality Assurance Laboratory. The counting efficiency was compared to a curve of efficiency vs. energy determined with a mixed gamma-ray emitter source obtained from NBS.

To test barium sulfate carrier recovery, various amounts of carrier, sample, and hydrochloric acid were used. Periods of boiling and settling were also varied. Both Atlanta tap water and demineralized water were tested. The barium carrier was standardized by quantitatively precipitating barium sulfate in triplicate and weighing barium sulfate under conditions identical to the tests.

Tracer tests were performed with the same EPA standard solutions used separately for radium-226 and radium-228, at concentrations of 1 - 25 pCi/L. The tracer was added to the sample and stirred before adding sulfuric acid. The net count rates were converted to pCi/L by dividing by the counting efficiency per peak, the conversion factor of 2.22 disintegrations per min per pCi, and the sample volume. The standard deviation due to counting uncertainty was based on the square root of the total count and the background count combined for both peaks.

Several EPA intercomparison solutions that contained both radium-

226 and radium-228 were analyzed after increasing their volumes to 3.8 L and adjusting the acidity to 0.2 N in HCl. Blank samples and samples of public water supplies also were analyzed as described above. Comparison values for the latter were obtained by using method 904.0 of the Prescribed Procedures (Krieger and Whittaker 1980).

Tests with tracer, intercomparison, and blank samples were performed in replicate. In some instances, samples were repeatedly counted in order to compare the observed standard deviation with the standard deviation of counting.

RESULTS AND DISCUSSION

The fraction of barium sulfate recovered as precipitate decreased with increasing sample volume, as would be anticipated. This loss could be counteracted by increasing the amount of added barium carrier, as shown in Table 2. When sufficient barium was added to form 84 mg barium sulfate, an average 97 percent was recovered under the specified precipitation conditions, with a range of 94 to 99 percent in eight trials. Tracer radium recovery was consistent with these barium yields.

The yields decreased severely when the highly acidified US EPA intercomparison study samples were analyzed. The tests of precipitate recovery vs. acidity shown in Table 2 indicated the importance of maintaining the acidity in the range of 0.1 to 0.2 normal and partially neutralizing samples that are excessively acid. Further

tests also indicated the importance of boiling the solution for an extended period to maintain high precipitate recovery.

The peak detection efficiencies in Table 3 were determined for the listed characteristic peaks of radium-228 and radium-226 progeny. The samples used for calibration contained near 500 pCi and were counted for 50,000 s. The counting efficiencies of the 338 keV and 352 keV gamma rays were consistent with calibrations obtained earlier as a function of energy in this configuration. Values were lower than predicted for the 609 keV and 911 keV gamma rays, presumably because coincidences with other gamma rays in cascade reduced the fraction of detected gamma rays.

The gamma ray fractions in Table 3, which are used in combination with the peak detection efficiencies to compute radium concentrations from peak net count rates, were obtained from a recent compilation (Martin 1985). Some differences still exist with other compilers, but these are less than 10 percent for the indicated gamma rays.

The background count rates given in Table 3 are summarized from the averages in Table 4, adjusted to the counting period of 6,000 s. These peak background averages are subtracted from gross counts to eliminate the contribution of radium progeny in the vicinity of the detectors. The continuum background values are listed only to indicate their magnitude; the actual values subtracted were obtained from each spectral analysis.

The mean values in Table 4 are for ten week-end measurements of the detector background at the four characteristic gamma rays. All background values except for the peaks at 338 and 911 keV fluctuated much more than predicted by the statistics of the accumulated counts. The excess over the predicted standard deviation is attributed to variation of radon-222 concentrations in room air and the resulting variation in lead-214 and bismuth-214 deposited near the detector (Kloke et al. 1965). The measurement indicated by an asterisk deviated by more than three standard deviations from the mean in some instances and was not used to calculate the mean, but indicates the extent to which ambient levels of radioactivity can influence the radiation background.

The peak counting efficiencies and the background mean values and standard deviations in Table 3 were used to compute the 1.96-sigma (95 percent confidence) level of the net count rate which is specified as the detection limit (US EPA 1976). As shown in Table 5, this value is 1.2 pCi/L for radium-228 and 1.0 pCi/L for radium-226 when a 3.8-L water sample is analyzed, the chemical recovery by precipitation is 97 percent, and the counting period is 6,000 s. Both characteristic peaks must be used for each isotope to attain this limit. At a concentration of 5 pCi/L, the 1.96-sigma value is approximately 2 pCi/L for radium-228 and 1 pCi/L for radium-226.

Radium analyses of blank barium sulfate precipitates on glass fiber filters held in 5-cm-diameter stainless steel planchets showed no significant radium-228 levels, but radium-226 levels were above

detection limits (see Table 6). The net count rates of 0.3 count/min each for the 352 and 609 keV gamma rays were due to the planchets. For subsequent measurements, therefore, filters with precipitates were sealed in plastic envelopes.

A series of tracer tests with standard radium solutions, performed separately with radium-226 and radium-228, resulted in measured values generally consistent with the amounts added. Table 7 lists results obtained in the range of 0 to 25 pCi/L, appropriate to the levels generally encountered in water supplies. Each entry is for a separate sample, except that one of the radium-228 samples that contained 1.1 pCi/L was counted eight times. For this series of measurements, the resulting 2-sigma value of 1.4 pCi/L is consistent with values of 1.1 to 1.3 pCi/L based on counting statistics. Of the 20 samples, 2 measurements differed by more than the 2-sigma value from the tracer concentrations.

The possibility of mutual interference was examined by determining the concentration of radium-228 in a sample that contained only radium-226, and vice versa. No gamma rays with energies that would interfere are known. As shown in Table 8, duplicate analyses resulted in one positive and one negative result in each set. At the MCL of 5 pCi/L for radium, the observed level due to mutual interference of the other isotope would be negligible.

Multiple samples of intercomparison study solutions that had been

distributed earlier by the US EPA were analyzed with the results given in Table 9. Radium-228 analyses have measured 2-sigma values of 3 pCi/L in the concentration range of 6 to 17 pCi/L and are within 2 sigma of the known values. The observed 2-sigma values are approximately 1.5 times the estimation for counting statistics. An approximately 2-fold larger analytical standard deviation compared to the standard deviation of counting has been observed in radiochemical analyses (Cline et al. 1983).

Radium-226 results, on the other hand, were consistently higher than values that had been reported for the US EPA intercomparison solutions. At the lowest concentration, the mean of measured values was within the 2-sigma value, but the two higher concentrations were outside this range. The cause of these higher measured values has not yet been determined. As in the case of radium-228, the observed 2-sigma values were about 1.5 times the estimated 2-sigma counting error.

Three samples of public water supplies that had been analyzed for radium with NIPDW Regulation methods (Krieger and Whittaker 1980) because of elevated gross alpha particle activity were also analyzed by gamma-ray spectral analysis. As indicated in Table 10, two samples did not contain detectable levels of radium-228 according to both methods. Two radium-226 results and one radium-228 result agreed, but for one sample the gamma-ray spectral analysis of radium-226 was higher than analysis by radon emanation. This sample contained elevated levels of uranium, but that radionuclide does not

interfere with the two characteristic radium-226 gamma-ray peaks.

SUMMARY AND CONCLUSIONS

Gross beta particle activity measurement can be used as a screening method for radium-228. One approach is to use the same sample for gross alpha and beta particle activity measurement. However, a larger sample volume must be evaporated or the counting period must be extended because the higher beta particle background count rate in conventional detectors results in a higher detection limit. The sample volume is limited by the amount of dissolved solids, which attenuate alpha and beta particles. As an alternative, radium can be collected from a larger volume of water by coprecipitation to eliminate dissolved solids. Various beta-particle detectors can be used, including gas ionization and liquid scintillation counters.

Gamma-ray spectral analysis is recommended as a better method because it permits simultaneous measurement of radium-228 and radium-226, and eliminates most false positive identifications. This approach has been used by several laboratories. Essentially the entire 3.8-L sample that is currently collected must be concentrated to attain specified detection limit ($1.96\text{-}\sigma$) of 1 pCi/L with a conventional Ge(Li) detector and a 6,000-s counting period. A smaller sample can be used if the detector is more efficient or the counting period is longer.

This method, using barium sulfate precipitation for concentration, was found to meet the specified detection limit in tests with radioactive tracers. Conditions suitable for almost complete collection of radium by precipitation were specified. The two isotopes do not interfere with each other in the analysis at MCL values.

The concentration and counting procedures are simple, brief, and use equipment that is widely available. A 1.5-d wait is required for 98-percent ingrowth of progeny of radium-228, and 22 d for the ingrowth of radium-226 progeny. Standard deviations observed in replicate measurements exceed the calculated value based on counting by about 50 percent, as had been found for other radiochemical procedures.

The method should now be tested for a wide range of water samples to check for chemical or radioactive interferences. The cause of some elevated radium-226 results must also be determined.

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Table 1. Estimated detection limits for radium-228 screening methods

Method Parameters	Collection Method and Radiation Detector			
	Evaporation; Prop. counter	Pption; Prop. counter	Pption; LS counter	Pption; Ge spectr.
Sample volume, L	0.2	0.4	1.0	4.0
Chemical yield	1.0	0.9	0.9	0.9
Radiation fraction	1.0	1.0	1.0	0.4
Counting efficiency	0.34	0.4	0.7	0.05
Counting period, min.	300	100	100	100
Background, c/min	1.2	1.2	30	0.3
Detection limit, pCi/L	1.2	1.0	1.1	1.1

Notes:

1. Pption = precipitation
Prop. counter = proportional counter
LS counter = liquid scintillation counter
Ge spectr. = germanium detector with spectrometer
2. LS counter channel C used
3. Ge spectr. utilizes gamma-ray peaks at 338 and 911 keV; radiation fraction and background values are combined for both gamma rays; counting efficiency is average value for the two gamma rays
4. Detection limit is 2-sigma (95%) counting error

Table 2. Barium sulfate recovery

Amount BaSO ₄ , mg	Sample volume, L	HCl, N	Recovery, % mean (range;no.)
28	2.0	0.24	92(85-98;8)
	3.0		88(77-96;8)
56	1.0		100(96-103;8)
	2.0		100(98-102;8)
	3.0		98(95-100;8)
	3.5		98(90-103;8)
	3.8		94(84-103;16)
84	3.8	0.06	95(93-97;4)
		0.12	97(96-97;2)
		0.24	97(94-99;8)
		0.48	90(89-90;2)
		0.72	71(66-77;4)

Table 3. Detector characteristics for counting radium-228 and radium-226

Isotope	Gamma-ray energy, keV	Gamma-ray fraction, %	Peak detection efficiency, %	Background count/6000 s	
				continuum	peak
Ac-228	338.4	11.3±0.3	6.6	15±4	3±1
Ac-228	911.1	26.6±0.7	2.5	7±3	3±1
Pb-214	351.9	35.4±0.3	6.4	18±4	15±6
Bi-214	609.3	44.8±0.4	3.1	12±3	11±5

Table 7. Tracer tests of radium analysis

<u>Radium-228, pCi/L</u>		<u>Radium-226, pCi/L</u>	
<u>added</u>	<u>measured</u>	<u>added</u>	<u>measured</u>
0	0±1.1		
1.1	2.6±1.3	1.2	1.3±0.8
	2.1±1.3	1.2	0.5±0.8
	1.1±1.3		
	1.1±1.3		
	0.4±1.1		
	1.3±1.3		
	0.8±1.1		
	1.1±1.3		
	<u>1.3±1.4</u>		
1.1	1.6±1.6		
1.8	1.1±1.1	1.8	1.3±0.8
1.8	3.2±1.6	1.8	2.1±0.8
2.9	1.9±1.3	2.4	2.6±0.8
3.4	1.6±1.3	2.3	1.7±1.8
		4.8	4.5±1.3
		4.9	4.8±1.1
22.	23±3	25.	23±2
22.	21±3	25.	29±2

Table 9. Analysis of EPA radium intercomparison samples

Sample date	<u>Radium-226, pCi/L</u>		<u>Radium-228, pCi/L</u>	
	EPA	This method	EPA	This method
091286	6.1	5.8 7.4 8.1 15.5* <u>7.2</u> 7.1±1.9	9.1	9.0 10.8 6.9 7.6 <u>8.9</u> 8.6±3.0
062086	8.6	12.2 11.6 11.2 10.9 9.0 <u>12.0</u> 11.2±2.3	16.7	13.2 13.6 14.7 15.5 10.8 <u>14.7</u> 13.8±3.4
091187	9.7	11.2 13.2 13.0 15.5 <u>13.2</u> 13.7±2.4	6.3	5.6 7.5 5.8 <u>8.4</u> 6.8±2.7

* Value is excluded from mean and standard deviation

Note: plus/minus values are 2 sigma

Table 10. Analysis of public water supplies for radium

Sample No.	Gross alpha particle activity, pCi/L	<u>Radium-226, pCi/L</u>		<u>Radium-228, pCi/L</u>	
		Current method	This method	Current method	This method
WS6889	60±3	2.6±1.1	4.6±0.9	1.0±1.2	1.3±1.3
WS6896	9±2	5.9±0.1	5.9±1.0	<1.	< 1.3
WS6916	4±1	2.4±0.1	2.6±0.9	<1	< 1.3

Notes: 1. Sample WS6889 contained mostly uranium
 2. Plus/Minus values are 2 sigma

Table 5. Calculated standard deviation of measuring 3.78 liter samples at radium concentrations of 1 and 5 pCi/l.

Gamma-ray energy, keV	net counts/6,000s		gross counts/6,000s		s.d./6,000s		2.s.d, pCi/l	
	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi
<u>Radium-228 at equilibrium</u>								
338	5.8	28.9	24	47	5.8	7.5	2.0	2.6
911	5.1	25.7	14	35	4.0	6.1	1.6	2.4
combined	—	—	—	—	—	—	1.2	1.7
<u>Radium-226 at equilibrium</u>								
352	17.6	87.9	53	123	10.2	13.2	1.2	1.5
609	10.8	53.9	38	81	8.2	10.4	1.5	1.9
combined	—	—	—	—	—	—	1.0	1.2

- Notes:
1. net counts = pCi x 6,000 x 0.037 x 0.97 x e x f
where e = counting efficiency, f = gamma fraction, and 0.97 is average chemical recovery.
 2. gross counts = net counts plus background continuum and peak.
 3. standard deviation (s.d.) per 6,000 s count = $(\text{gross count} + \text{s.d. (continuum)}^2 + \text{s.d. (peak)}^2)^{0.5}$.
 4. 2 s.d. value in pCi/l = 2 x s.d. per 6,000-s count (6,000 x 0.037 x 0.97 x 3.78 ef).
 5. The s.d. for measuring one of the radium isotopes with two gamma rays is: $(\text{s.d.})^2_{\text{combined}} = 0.5 (\text{s.d.})_1^2 + 0.5 (\text{s.d.})_2^2$

Table 6. Radium analysis of blank water samples

	Sample 1	Sample 2	Sample 3
<u>Ra-228</u>			
338-keV, counts/6,000s	4.5 \pm 12	6.5 \pm 10	3.7 \pm 10
911-keV	1.2 \pm 6.6	0.6 \pm 7.3	3.1 \pm 8.7
338-keV, pCi/gallon	2.6 \pm 7.0	4.0 \pm 6.2	2.2 \pm 6.0
911-keV	0.8 \pm 4.4	0.4 \pm 5.1	2.2 \pm 6.2
both	1.7 \pm 4.1	2.2 \pm 4.0	2.2 \pm 4.3
average, pCi/liter	0.5 \pm 1.1 (\pm 0.1)		
<u>Ra-226</u>			
352-keV, counts/6,000s	26 \pm 18	32 \pm 19	24 \pm 19
609-keV	3.1 \pm 13	41 \pm 19	41 \pm 18
352-keV, pCi/gallon	5.6 \pm 3.8	6.4 \pm 3.9	5.0 \pm 3.9
609-keV	1.1 \pm 4.6	13.5 \pm 6.2	13.7 \pm 6.2
both	3.4 \pm 3.0	10.0 \pm 3.7	9.3 \pm 3.7
average, pCi/liter	2.0 \pm 0.9 (\pm 1.0)		
chemical yield, %	90.9	95.7	94.3

Note: Plus/minus values are 1 standard deviation of counting; for the average values, the first plus/minus value is the average standard deviation for the three measurements, while the value in parentheses is the value calculated from the three measurements.

Table 4. Detector background counts per 200,000 seconds

Date	Radium-226		Radium-226		Radium-228		Radium-228	
	352 keV		609 keV		338 keV		911 keV	
	Cont.	Peak	Cont.	Peak	Cont.	Peak	Cont.	Peak
9-4-87	434	233	363	301	437	127	215	72
9-11-87	520	555	472	348	583	143	315	150
9-18-87	716	471	464	342	673	115	279	78
9-25-87	686	570	411	454	565	99	274	99
10-2-87	562	562	351	491	554	89	271	102
10-2-87*	758	927	470	744	766	174	350	124
6-24-88	489	684	429	472	333	103	188	87
7-8-88	774	607	358	472	327	99	155	142
7-22-88	590	356	380	250	546	124	188	78
7-22-88	528	373	350	303	589	69	164	146
Mean*	589	590	398	381	512	108	228	106
S.D.	113	144	48	91	120	22	57	32
S.D. counting	24	41	20	34	23	34	15	24
No. of channels - at 0.5 keV/channel	-	6	-	6	-	4	-	5

* Data for 10-9-87 were omitted in calculation mean values and standard deviations.

Note: S.D=standard deviation

Table 8. Interferences in characteristic peaks

<u>Activity added, pCi/L</u>		<u>Activity measured, pCi/L</u>	
<u>Ra-226</u>	<u>Ra-228</u>	<u>Ra-226</u>	<u>Ra-228</u>
25	0	-	0.7
25	0	-	- 0.3
0	25	1.5	-
0	25	- 0.2	-

E-25-m16

Final Technical Report
Screening Method for Radium-228 in Drinking Water

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ABSTRACT

Methods for measuring radium-228 were reviewed to select a brief and simple screening procedure under NIPDW Regulations for public water supplies. A two step method was considered to concentrate radium by evaporation or precipitation and to count it with a gas-filled proportional (or Geiger-Mueller) detector, a liquid scintillation detector, or a germanium detector with multichannel analyzer.

Gross beta particle counting appears to be feasible for screening to meet the 1 pCi/L detection limit. One can utilize the same sample volume as currently collected and measure radiation with commonly available equipment in reasonable time periods. The required sample volumes and counting periods were estimated on the basis of known counting efficiencies and background count rates.

Gamma-ray spectral analysis is the recommended option, however, because radium-226 and radium-228 can be determined directly and simultaneously. Several aspects of the method were examined to assure that the concentration procedure is nearly quantitative and that the detection limit can be reached with a 3.78-L sample in a 6,000-s counting period. The method was tested with radium tracer solutions, EPA intercomparison samples, water supply samples, and blanks and was found appropriate for radium-228 and radium-226 analyses over the range of 1 to 25 pCi/L.

Keywords: Radium-228, radium-226, water analysis, gamma-ray spectral analysis.

INTRODUCTION

More than 50,000 community water systems in the U.S. are monitored in 4-year cycles to determine whether the combined content of radium-226 and radium-228 exceeds the maximum contaminant level (MCL) of 5 picocuries per liter (pCi/L). Because radium analyses are relatively labor intensive, the National Interim Primary Drinking Water (NIPDW) Regulations provide a screening procedure according to which radium-226 must be measured only if the gross alpha particle activity exceeds 5 pCi/L. Radium-228 must then be measured if radium-226 exceeds 3 pCi/L (US EPA 1976). Gross alpha particle activity screening measures the alpha particles emitted by radium-226; screening for radium-228 was justified by the belief that only rarely would the concentration of radium-228 exceed that of radium-226 (US EPA 1976). Data subsequently obtained during the nationwide monitoring program has invalidated this belief (Blanchard et al. 1985), and stimulated the present search for a measurement procedure for radium-228 in water, either by screening or brief and simple analysis.

The prescribed procedure for radium-228 analysis (Krieger and Whittaker 1980) under the NIPDW Regulations consists of

precipitating radium with combined barium and lead sulfates from an acidified 1-liter sample. Interferences are removed by selectively precipitating and dissolving sulfates in the presence of a complexing agent and by lead sulfide scavenging. After storage for at least 1.5 days to permit ingrowth of the 6.13-h actinium-228 daughter of 5.76-y radium-228, actinium-228 is coprecipitated from the purified solution with yttrium carrier, first as hydroxide and then as oxalate. The actinium-228 is immediately counted with a low-background gas-filled proportional or Geiger-Mueller detector. Chemical yields for radium and actinium are determined by weighing the barium sulfate and yttrium oxalate precipitates. Another procedure provides alternatives for separation and purification by solvent extraction, and depends on reproducibly high recovery instead of measuring yields (Percival and Martin 1974).

This study surveyed available procedures for their applicability for screening or simple analysis, estimated some parameters to determine whether the four more promising approaches would meet the criteria for such use, and then checked a selected procedure. The criteria were that the analysis could be performed with the currently collected 1-gallon (3.78-L) water sample by laboratories that now analyze these samples, with a detection limit of 1 pCi/L at the 95% confidence level of present procedures (US EPA 1976). A laboratory was expected to process approximately 20 samples per week plus associated quality control samples, and to measure them with available radiation detectors.

METHODS REVIEW

Noyce (1980), in reviewing radium-228 analytical methods for water samples published from 1967 to 1980, described several that are the precursors of the above-cited methods for separating first radium and then actinium, and counting actinium-228 beta particles with a gas-ionization detector. Radioactive interferences in drinking water samples were mainly other uranium- and thorium-chain radionuclides. Initial concentration and purification were also achieved by sorption on manganese-dioxide-coated filters or by precipitating ferric hydroxide and barium sulfate. Further purification was by repeated precipitations, solvent extraction or ion exchange. For radiation detection, liquid scintillation (LS) counting, alpha particle spectrometry (for the 1.91-y thorium-228 daughter of actinium-228 which slowly grows into purified radium-228), and beta-gamma coincidence counting of actinium-228 were also used.

Methods development along these lines has continued. Brooks and Blanchard (1980) purified radium by solvent extraction after an initial barium sulfate precipitation. Krieger and Whittaker (1980) describe gross beta counting of an evaporated water sample. Lieberman (1984) precipitated mixed ferric hydroxide and barium sulfate for gross activity screening. Henry (1982) and Bivens (1986) concentrated radium by barium sulfate precipitation and determined radium by gamma-ray spectrometry. Lucas (1987)

concentrated radium on a radium-selective complexing resin. Velten (1983) converted barium sulfate first to the carbonate and then to the acetate to obtain radium soluble in an organic LS cocktail. Godoy and Schuettelkopf (1983) counted Cherenkov radiation from an aqueous solution of radium in a liquid scintillation detector. McCurdy and Mellor (1981) expanded their coincidence technique to determine actinium-228 by beta-gamma coincidences and radium-226 by alpha-gamma coincidences.

The four approaches listed in Table 1 were selected from these procedures to consider screening for the presence of radium-228 at levels that, combined with radium-226, would exceed the MCL. Each approach consists of only two steps -- concentration and radioactivity measurement. The sample volumes and counting times required to achieve a detection limit of 1 pCi/L were estimated on the basis of counting efficiencies, background count rates, and chemical yields observed at this laboratory. The precipitate was assumed to be barium sulfate, although other concentration procedures cited above could be substituted. The elegant coincidence counting procedure was not considered because the detection system is believed to be much less commonly available than gas-ionization, liquid scintillation, and germanium detectors in laboratories that perform routine radionuclide measurements.

Sample evaporation and subsequent gross beta particle counting can be combined with the currently applied gross alpha particle activity screening. The energetic beta particles of actinium-228

and possibly some weak beta particles of radium-228 are counted. In detection systems with pulse height discrimination, the beta-particle count can be obtained simultaneously with the alpha-particle count. In other systems, alpha and beta particles are counted together, and alpha particles are then counted by themselves at a lower applied voltage. This screening approach is limited by alpha and beta particle absorption in sample solids. If the dissolved solids content is below 0.3 gram/L, a 0.35 L sample can be evaporated and the counting period can be reduced. On the other hand, a dissolved solids content above 0.5 gram/L will require a smaller sample volume, balanced by counting longer than 300 minutes.

Concentration by coprecipitation eliminates dissolved solids and can provide uniform sample weight with small and consistent self-absorption for alpha and beta particles. A 0.4-L sample permits counting with a proportional or Geiger-Mueller detector for the 100-minute period considered suitable for handling the normal sample load. Larger sample volumes would improve precision at the MCL value or permit briefer measurements. Because the precipitate does not carry all radionuclides, it would not provide the same broad-spectrum radionuclide screening as evaporated samples. This separation is beneficial if screening is only for radium, but might require modifications if other radionuclides, such as uranium, should be included in the screening.

The concentration steps must be quantitative unless the yield

can be measured for a non-isotopic carrier. When barium sulfate is the carrier, the recovery of radium exceeds that of barium, but varies with precipitating conditions (Kirby and Salutsky 1964), hence near-quantitative yields are required to minimize the uncertainty in yield.

Liquid scintillation counting after precipitation requires more sample because the LS detector has a higher background count rate than anticoincidence gas ionization detectors (see Table 1). The sample volume and counting period can be reduced by improving the LS system, the selected channel width, the procedure used for dissolving or dispersing the solid in the scintillation cocktail, and the choice of cocktail (or use of Cherenkov counting in an aqueous solution). These decisions will also determine whether one counts actinium-228, radium-228 or both, and what radiations may interfere.

False positive identification of radium-228 can be expected in all three approaches if other radionuclides that emit beta particles are in the sample. Some interferences can be eliminated by precipitation, volatilization during evaporation, and energy discrimination. Combined alpha- and beta-particle measurements can identify some interfering radionuclides, and repeated measurements can assist by observing the rate of radioactive ingrowth or decay. Even taking this information into account, samples that could have concentrations above the MCL value will then have to be analyzed for radium-226 and radium-228.

Gamma-ray spectral analysis with a germanium detector can eliminate most interferences. Hence, this is a direct analytical procedure for both radium-226 and radium-228. A much larger sample volume is needed because the typical detector has a relatively low counting efficiency and the characteristic gamma rays used to identify and measure these radionuclides have low decay fractions. Because these gamma rays are emitted by short-lived radioactive progeny, ingrowth periods after precipitation of 1.5 days and 22 days, respectively, are required before these radium-228 and radium-226 progeny, once separated, reach 98 percent of equilibrium.

In view of its simplicity and potential for direct analysis, gamma ray spectrometry after radium concentration was selected for experimental study. Several variants of this approach are already in use (Michel et al. 1981, Henry 1982, Bivens 1986, Lucas 1987). The marginal sensitivity of the procedure, indicated by use of the entire 3.78-L sample to attain the detection limit of 1 pCi/L, is the major concern in recommending it for nationwide monitoring. Studies were undertaken to assure high chemical yields for the barium sulfate precipitation, examine the variability in detector background due to airborne radon daughters, and test the agreement of observed concentrations and standard deviations of measurement near the MCL with values predicted for standard solutions and radioactive tracers.

ANALYTICAL PROCEDURES

The 3.78-L sample is preserved by adding 60 ml 1 N nitric acid (Krieger and Whittaker 1980). To precipitate barium sulfate, the sample is further acidified with 20 ml concentrated (12 N) hydrochloric acid; 5 ml barium carrier (88 mg $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) is pipetted into the solution and mixed with it; and 20 ml 18 N sulfuric acid is added. The solution is heated to boiling while being stirred, boiled gently for 30 minutes, and then stored overnight to let the precipitate settle. The precipitate is collected on a tared glass fiber filter (Gelman type A/E, 47 mm dia.) clamped in a filter funnel. The filter is washed with 10 ml ethanol and 10 ml diethyl ether under vacuum suction and then dried approximate 30 min. under a heat lamp. The filter with precipitate is weighed to determine the yield. At 100 percent yield, the weight of barium sulfate is 84.0 mg. An average weight loss by the filter of 0.6 mg was found when filtering 3.78 L of water.

The filter, placed in a stainless steel planchet, is counted on the window of a Ge(Li) detector. The detector is a right circular cylinder 60 mm long and 53 mm in diameter drifted coaxially with the closed end at the thin aluminum window. Its nominal efficiency at 1.332 MeV is 24.6% relative to a NaI(Tl) detector, with a full width at half maximum of 1.9 keV. The spectrum is collected with a 4,096-channel analyzer at 0.5 keV per channel. Detector and sample are shielded by 10-cm thick lead

with a 2-mm copper liner except where the cryostat from the liquid-nitrogen dewar flask passes through the shield.

Each sample is counted for 6,000 s. The count rates under two characteristic photoelectric peaks each are determined to measure radium-228 and radium-226. The radiation background due to the Compton continuum from more energetic gamma rays in the sample and from the environment is determined from count rates on both sides of each peak, and is subtracted from the gross count rate of each peak. In addition, the count rate of the natural radiation background peak at each characteristic energy is determined by counting for 200,000 s every weekend, and these values are also subtracted from the gross count rates.

The sample activity is calculated from the net count rate at each peak by dividing by the peak detection efficiency, the gamma ray fraction, the sample volume and the barium recovery fraction. Results for the two characteristic peaks are averaged.

Samples are counted after waiting for progeny ingrowth periods of at least 1.5 d in radium-228 and 22 d in radium-226. Ingrowth periods for radium-226 can be reduced by calculating the fractional ingrowth of 3.82-d radon-222 and its progeny, but this change increases the detection limit.

The detection efficiency of the characteristic peaks was determined by counting barium sulfate from samples to which

standard solutions of either radium-226 or radium-228 had been added. These NIST standard solutions were obtained from the US EPA EMSL Las Vegas Quality Assurance Laboratory.

To test barium sulfate carrier recovery, various amounts of carrier, sample, and hydrochloric acid were added to Atlanta tap water or demineralized water. The specified amount of sulfuric acid was added to each sample. Periods of boiling and settling were varied initially and then maintained as described. The barium carrier was standardized by quantitatively precipitating barium sulfate in triplicate and weighing barium sulfate under conditions identical to the tests.

Tracer tests were performed with the same standard solutions added to acidified water separately for radium-226 and radium-228, at concentrations of 1 - 25 pCi/L. The standard deviation due to counting uncertainty was calculated as the square root of the total count and the background count combined for both peaks.

Several EPA intercomparison solutions that contained both radium-226 and radium-228 were analyzed after increasing their volumes to 3.78 L and adjusting the acidity to 0.2 N in HCl. Blank samples and samples of public water supplies also were analyzed as described above. Comparison values for the latter were obtained by using methods 903.1 and 904.0 of the Prescribed Procedures (Krieger and Whittaker 1980).

Tests with tracer, intercomparison, and blank samples were performed in replicate. In some instances, samples were repeatedly counted in order to compare the observed standard deviation of results with the standard deviation of counting.

RESULTS AND DISCUSSION

The fraction of barium sulfate recovered as precipitate decreased with increasing sample volume, as would be anticipated. This loss was counteracted by increasing the amount of added barium carrier to the extent shown in Table 2. When sufficient barium was added to form 84 mg barium sulfate, an average 97 percent was recovered under the described precipitation conditions, with a range of 94 to 99 percent in eight trials. The yield is somewhat less than predicted under ideal conditions. At the specified barium and sulfate concentrations in the sample, a barium sulfate solubility product of 2×10^{-10} in water at 50°C (Weast, 1978) would result in a 99.5 percent yield.

The yield decreased severely when the highly acidified US EPA intercomparison study samples were analyzed. The tests of precipitate recovery vs. acidity shown in Table 2 indicated the importance of maintaining the HCl concentration between 0.1 and 0.2 normal. Further tests also indicated the importance of boiling the solution for the indicated period to recover the precipitate to the extent shown.

Time series studies with tracers determined the accumulation or decay pattern of the radioactive progeny whose gamma rays were counted. Approximately 500 pCi of radium-226 or radium-228 were added to separate solutions, and the precipitates were counted to determine ingrowth rates.

Although barium sulfate is known to retain radon-222 very effectively (Kirby and Salutky 1964), completeness of ingrowth of radon-222 into radium-226 in freshly precipitated barium sulfate was tested by counting the lead-214 352-keV gamma ray on four occasions. As shown in Figure 1, the ingrowth measurements agree with the ingrowth curve for the radon-222 half life of 3.82 d. Any significant loss of radon-222 by emanation would produce more rapid ingrowth and lower equilibrium count rates.

Measurements of precipitated barium sulfate with radium-228 that initially had its progeny in equilibrium suggest that actinium-228 is completely coprecipitated with barium sulfate. An actinium-228 measurement 1 h after filtering the precipitate and 5 h after precipitation was identical, within counting statistics, with a second measurement performed 2 days later. Such retention eliminates the need for a time interval between sample preparation and counting, although a 2-day interval had been used in this study.

The count rates of the lead-212 and thallium-208 gamma rays in the radium-228 sample, counted from 1 h to 14 d after

filtration had a long-lived component of approximately 25 percent. This observation suggested that 21 percent of thorium-228 was carried by barium sulfate. Unsupported radium-224 and its progeny lead-212 and thallium-208 decayed with its 3.6-d half life. Hence, these gamma rays are not suitable for measuring radium-228 within a few days of concentration, although their relatively high intensities would otherwise be helpful in detecting radium-228.

The detection efficiencies for photoelectric peaks in Table 3 were determined for the listed characteristic peaks of radium-228 and radium-226 progeny. The samples used for calibration contained approximately 500 pCi and were counted repeatedly for 6,000-s periods. The counting efficiencies of the 338 keV, 352 keV, and 911 keV gamma rays were consistent with calibration obtained as a function of energy between 186 and 911 keV in this configuration (see Figure 2). A lower efficiency for the 609 keV gamma ray is attributed to coincidences with other bismuth-214 gamma rays in cascade.

The gamma ray fractions in Table 3, which are used in combination with the peak detection efficiencies to compute radium concentrations from peak net count rates, were obtained from a recent compilation (Martin 1985). Some differences still exist with other compilers, but these are 10 percent or less for the four gamma rays.

Mean detector background values (see Table 4) were obtained from ten week-end measurements of the four characteristic gamma rays. All background values except for the actinium-228 peaks at 338 and 911 keV fluctuated much more than predicted by the statistics of the accumulated counts. The excess over the predicted standard deviation is attributed to variation of radon-222 concentrations in room air resulting in different amounts of lead-214 and bismuth-214 deposited near the detector (Kloke et al. 1965). The measurements indicated by an asterisk deviated by more than three standard deviations from the mean and were not used to calculate the mean, but indicate the extent to which fluctuating ambient levels of radon-222 progeny can influence the radiation background.

The average detector background count rates from Table 4 are summarized in Table 5, adjusted to the counting period of 6,000 s. The continuum background values are listed only to indicate their magnitude; the actual subtracted values were obtained from each spectral analysis. Also given in Table 5 are backgrounds at the peaks due to the Compton continuum from higher-energy gamma rays emitted by radium-226 and radium-228 progeny. These do not contribute significantly to the background and the standard deviation of the concentration values near the detection limit, but increase the measurement uncertainty at higher concentrations.

The counting efficiencies at the characteristic peaks, Compton continuum values at these peaks, and background peak standard

deviations were used to compute the 1.96-sigma (95 percent confidence) level of the net count rate which is specified as the detection limit (US EPA 1976). As shown in Appendix A and Table 5, the detection limit is 1.2 pCi/L for radium-228 and 0.7 pCi/L for radium-226 when a 3.78-L water sample is analyzed, the chemical recovery by precipitation is 97 percent, and the counting period is 6,000 s. Both characteristic peaks are used for each isotope to attain this limit. At a concentration of 5 pCi/L, the 1.96-sigma value is 1.6 pCi/L for radium-228 and 1.0 pCi/L for radium-226.

The typical detector background spectrum from 0 to 1024 keV in Figure 3 shows the magnitude of the background peaks at the four characteristic gamma ray energies. The 200,000-s collection period has a 6-fold better standard deviation per channel than the 6,000-s periods used for analyzing samples, reflected in a correspondingly narrower band of the background continuum. As indicated by the values in Table 5, a sample that contains radium-228 at 1 pCi/L would more than triple the height of the characteristic background peaks, while radium-226 at that concentration would approximately double the heights of these peaks.

Results of analyzing duplicate blank water samples, in Table 6, show concentrations below the detection limit of 1 pCi/L. Numerous measurements of water samples that contained no tracer suggest that the radium-228 background is near zero, but that

there is a consistent radium-226 background at 352 and 609 keV equivalent to about 0.5 pCi/L. The latter may be due to contamination of the steel planchets or deposition of radon-222 progeny on the filter.

High concentrations of radium-226 tracer yield a small peak at 338 keV but none at 911 keV. As shown in Table 6, this weak peak, attributed to a minor gamma ray from bismuth-214, would cause a false positive radium-228 result of approximately 1 pCi/L at a radium-226 concentration of 50 pCi/L when its progeny are at equilibrium, or less before radium-226 progeny reach equilibrium. Large amounts of radium-228 tracer, on the other hand, did not interfere with the radium-226 analysis at the detection limit of 1 pCi/L.

The series of duplicate tracer tests with standard radium solutions, shown in Table 7, performed separately with either radium-226 or radium-228, yield measured values consistent with the amounts added in the range of 0 to 25 pCi/L. When the radium-228 sample that contained 1.1 pCi/L was counted eight times, its observed 2-standard-deviation value was 1.4 pCi/L, compared to values of 1.1 to 1.3 pCi/L based on counting statistics. Of the 18 samples, 2 measurements differed by more than the 2-sigma value from the tracer concentrations.

The measurement results in Table 7 show no positive bias that could be attributed to significantly higher yields for radium than

barium, or to radium-226 contamination. Such bias would not be detectable at the indicated standard deviations, however, if the radium yield were only 1-2 percent higher or the contamination were about 2 pCi per sample (0.5 pCi/L).

Analyses of four to six replicate samples of three inter-comparison study solutions that had been distributed earlier by the US EPA gave results in agreement with EPA values (see Table 8). Radium-226 results averaged higher than EPA values by 0.7 pCi/L. One set of radium-228 analyses gave relatively widely varying results. For others, the observed 2-standard-deviation values are approximately twice the values estimated for counting statistics. The same ratio was observed previously in radiochemical analyses (Cline et al. 1983), and can be attributed to the effects of other physical and chemical procedures in the analysis. Only a small part of the elevated standard deviation should be due to the presence of a second radium radioisotope.

Three samples of public water supplies that had been analyzed for radium with NIPDW Regulation methods (Krieger and Whittaker 1980) because of elevated gross alpha particle activity gave consistent results by gamma-ray spectral analysis, as shown in Table 9. Two samples did not contain detectable levels of radium-228 according to both methods. The three radium-226 and one radium-228 results agreed within the indicated counting uncertainty.

SUMMARY AND CONCLUSIONS

Gross beta particle activity measurement can be used as a screening method for radium-228. One approach is to use the same sample for gross alpha and beta particle activity measurement. However, a larger sample volume must be evaporated or the counting period must be extended because the higher beta particle background count rate in conventional detectors results in a higher detection limit. The sample volume is limited by the amounts of dissolved solids, which attenuate alpha and beta particles. As an alternative, radium can be collected from a larger volume of water by coprecipitation or sorption to limit dissolved solids. Various beta-particle detectors can be used, including gas ionization and liquid scintillation counters.

Gamma-ray spectral analysis is recommended as a better method because it permits simultaneous measurement of radium-228 and radium-226, and eliminates false positive identifications associated with gross activity determinations. This approach has been used by several laboratories. Radium from almost the entire 3.78-L sample that is currently collected must be concentrated to attain the specified detection limit (1.96-sigma) of 1 pCi/L at a 6,000-s counting period with a conventional Ge(Li) or Ge detector. A smaller sample can be used if the detector is more efficient or the counting period is longer.

This method, with barium sulfate precipitation for concentration, was found to meet the specified detection limit in tests with radioactive tracers. Conditions suitable for almost complete collection of radium by precipitation were selected. The two isotopes do not significantly interfere with each other in analyses at MCL values.

The concentration and counting procedures are simple, brief, and use equipment that is widely available. The characteristic gamma rays of actinium-228 can be measured immediately after concentration to determine radium-228, while a 22-d waiting period is required for the ingrowth of radium-226 progeny. Standard deviations observed in replicate measurements are about 2-fold the calculated value based only on counting, as had been found earlier for other radiochemical procedures. The method should now be used for a wide range of water samples to check for chemical or radioactive interferences.

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Appendix A. Calculated standard deviation of measuring 3.78 liter samples at radium concentrations of 1 and 5 pCi/l

Gamma-ray energy, keV	net counts/6,000s		gross counts/6,000s		s.d./6,000s		2.s.d, pCi/l	
	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi	3.8pCi	19pCi
<u>Radium-228 at equilibrium</u>								
338	7.4	37.0	26	58	6.6	8.7	1.8	2.4
911	6.7	33.7	17	44	5.0	7.2	1.5	2.1
combined	—	—	—	—	—	—	1.2	1.6
<u>Radium-226 at equilibrium</u>								
352	22.6	113.0	56	148	9.5	13.6	0.8	1.2
609	13.2	66.0	36	90	7.5	10.6	1.1	1.6
combined	—	—	—	—	—	—	0.7	1.0

- Notes:
1. net counts = pCi x 6,000 x 0.037 x 0.97 x e x f
where e = counting efficiency, f = gamma fraction, and 0.97 is average chemical recovery.
 2. gross counts = net counts plus background continuum and peak.
 3. standard deviation (s.d.) per 6,000 s count = $(\text{gross count} + \text{continuum} + \text{s.d. (peak)}^2)^{0.5}$.
 4. 2 s.d. value in pCi/l = $2 \times \text{s.d. per 6,000-s count} / (6,000 \times 0.037 \times 0.97 \times 3.78 \text{ ef})$.
 5. The s.d. for measuring one of the radium isotopes with two gamma rays is: $(2\text{s.d.})^2 \text{ combined} = (\text{s.d.})_1^2 + (\text{s.d.})_2^2$
 6. Continuum count/6000 s due to compton interactions from higher-energy gamma rays is not insignificant.

Table 1. Estimated detection limits for radium-228 screening methods

Method Parameters	<u>Collection Method and Radiation Detector</u>			
	Evaporation; Prop. counter	Pption; Prop. counter	Pption; LS counter	Pption; Ge spectr.
Sample volume, L	0.2	0.4	1.0	4.0
Chemical yield	1.0	0.9	0.9	0.9
Radiation fraction	1.0	1.0	1.0	0.4
Counting efficiency	0.34	0.4	0.9	0.05
Counting period, min.	300	100	100	100
Background, c/min	1.2	1.2	30	0.3
Detection limit, pCi/L	1.2	1.0	0.8	1.1

Notes:

1. Pption = precipitation
Prop. counter = proportional counter
LS counter = liquid scintillation counter
Ge spectr. = germanium detector with spectrometer
2. LS counter channel C used
3. Ge spectr. utilizes gamma-ray peaks at 338 and 911 keV; radiation fraction and background values are combined for both gamma rays; counting efficiency is average value for the two gamma rays
4. Detection limit is 2-sigma (95%) counting error

Table 2. Barium sulfate recovery

Amount BaSO ₄ , mg	Sample volume, L	HCl, <u>N</u>	Recovery, % mean (range;no.)
28	2.0	0.24	92(85-98;8)
	3.0		88(77-96;8)
56	1.0		100(96-103;8)
	2.0		100(98-102;8)
	3.0		98(95-100;8)
	3.5		98(90-103;8)
	3.8		94(84-103;16)
84	3.8	0.06	95(93-97;4)
		0.12	97(96-97;2)
		0.24	97(94-99;8)
		0.48	90(89-90;2)
		0.72	71(66-77;4)

Table 3. Counting characteristics for radium-228 and radium-226

Isotope	Gamma-ray energy, keV	Peak Gamma-ray fraction, %	Detection efficiency, %
Ac-228	338.4	11.3 \pm 0.3	7.9
Ac-228	911.1	26.6 \pm 0.7	3.1
Pb-214	351.9	35.4 \pm 0.3	7.8
Bi-214	609.3	44.8 \pm 0.4	3.6

Table 4. Detector background counts per 200,000 seconds

Date	Radium-226				Radium-228			
	352 keV		609 keV		338 keV		911 keV	
	Cont.	Peak	Cont.	Peak	Cont.	Peak	Cont.	Peak
9 -4-87	434	233	363	301	437	127	215	72
9-11-87	520	555	472	348	583	143	315	150
9-18-87	716	471	464	342	673	115	279	78
9-25-87	686	570	411	454	565	99	274	99
10-2-87	562	562	351	491	554	89	271	102
10-9-87	758	927*	470	744*	766	174	350	124
6-24-88	489	684	429	472	333	103	188	87
7 -8-88	774	607	358	472	327	99	155	142
7-15-88	590	356	380	250	546	124	188	78
7-22-88	528	373	350	303	589	69	164	146
Mean	606	490	405	381	537	114	240	108
S.D.	120	144	51	91	138	31	67	30
S.D. counting	24	41	20	34	23	34	15	24
No. of channels at 0.5.keV/channel	-	6	-	6	-	4	-	5

* These data for 10-9-87 were omitted as outliers in calculating mean values and standard deviations.

Notes: S.D = standard deviation

Cont. = continuum beneath peak due to Compton scattering of more energetic gamma rays.

Table 5. Detection limits for 3.78-L sample in 6,000-s counting period

Gamma-ray energy, keV	Net counts for 1 pCi/L	Background counts			2 S.D. for 1 pCi/L, pCi/L	
		cont. from Ra-228	cont. from Ra-226	detector cont. peak		
<hr/>						
<u>Radium-228 at equilibrium</u>						
338	7.4	0.6	0.6	15	3+1	1.8
911	6.7	0.1	0.3	7	3+1	1.5
combined	—	—	—	—	—	1.2
<u>Radium-226 at equilibrium</u>						
352	22.6	0.9	0.4	18	15+4	0.8
609	13.2	0.5	0.2	12	11+3	1.1
combined	—	—	—	—	—	0.7

- Notes:
1. Compton continuum values are for the following peak widths: 2.0 keV at 338 keV; 2.5 at 911; 3.0 at 352; and 3.0 at 609.
 2. Detector background counts are from Table 4.
 3. All counts are for 6,000-s periods.
 4. S.D. = standard deviation.
cont.= Compton-scattering continuum.

Table 6. Interferences in characteristic peaks

<u>Activity added, pCi/L</u>		<u>Activity measured, pCi/L</u>	
Ra-226	Ra-228	Ra-226	Ra-228
0	0	0.1	-0.1
0	0	0.9	0.0
92	0	-	1.7
92	0	-	1.7
9	0	-	0.2
9	0	-	0.3
0	175	0.8	-
0	175	0.8	-

Table 7. Tracer tests of radium analysis

<u>Radium-228, pCi/L</u>		<u>Radium-226, pCi/L</u>	
added	measured	added	measured
1.1	2.6±1.3	1.2	1.3±0.8
	2.1±1.3	1.2	0.5±0.8
	1.1±1.3		
	1.1±1.3		
	0.4±1.1		
	1.3±1.3		
	0.8±1.1		
	1.1±1.3		
	1.3±1.4 avg.		
1.1	1.6±1.6		
1.8	1.1±1.1	1.8	1.3±0.8
1.8	3.2±1.6	1.8	2.1±0.8
2.9	1.9±1.3	2.4	2.6±0.8
3.4	1.6±1.3	2.3	1.7±1.8
		4.8	4.5±1.3
		4.9	4.8±1.1
22.	23±3	25.	23±2
22.	21±3	25.	29±2

Note: ± values are 2 standard deviations based on counting statistics, except that the ± value of the average value represents 2 standard deviations determined from replicate measurements.

Table 8. Analysis of EPA radium intercomparison samples

Sample date	Radium-226, pCi/L		Radium-228, pCi/L	
	EPA	This method	EPA	This method
121286	6.8±2.0	10.0	11.1±3.4	11.9
		6.6		11.3
		6.7		10.0
		<u>7.1</u>		<u>11.4</u>
		7.8±3.2		11.2±1.6
062086	8.6±2.6	9.2	16.7±5.0	15.7
		9.0		19.3
		10.0		17.2
		9.5		15.4
		7.1		9.6
		<u>9.5</u>		<u>15.3</u>
		9.1±2.0		15.4±6.4
091187	9.7±3.0	9.7	6.3±1.8	7.6
		10.3		6.4
		11.3		5.6
		<u>9.2</u>		<u>5.4</u>
		10.1±1.8		6.2±2.0

Note: plus/minus values are 2 standard deviations

Table 9. Analysis of public water supplies for radium

Sample No.	Gross alpha particle activity, pCi/L	<u>Radium-226, pCi/L</u>		<u>Radium-228, pCi/L</u>	
		Current method	This method	Current method	This method
WS6889	60±3	2.6±1.1	3.8±0.9	1.0±1.2	1.1±1.3
WS6896	9±2	5.9±0.1	4.8±1.0	<1	< 1.3
WS6916	4±1	2.4±0.1	2.1±0.9	<1	< 1.3

Notes: 1. Sample WS6889 contained mostly uranium
 2. Plus/minus values are 2 standard deviations of counting.

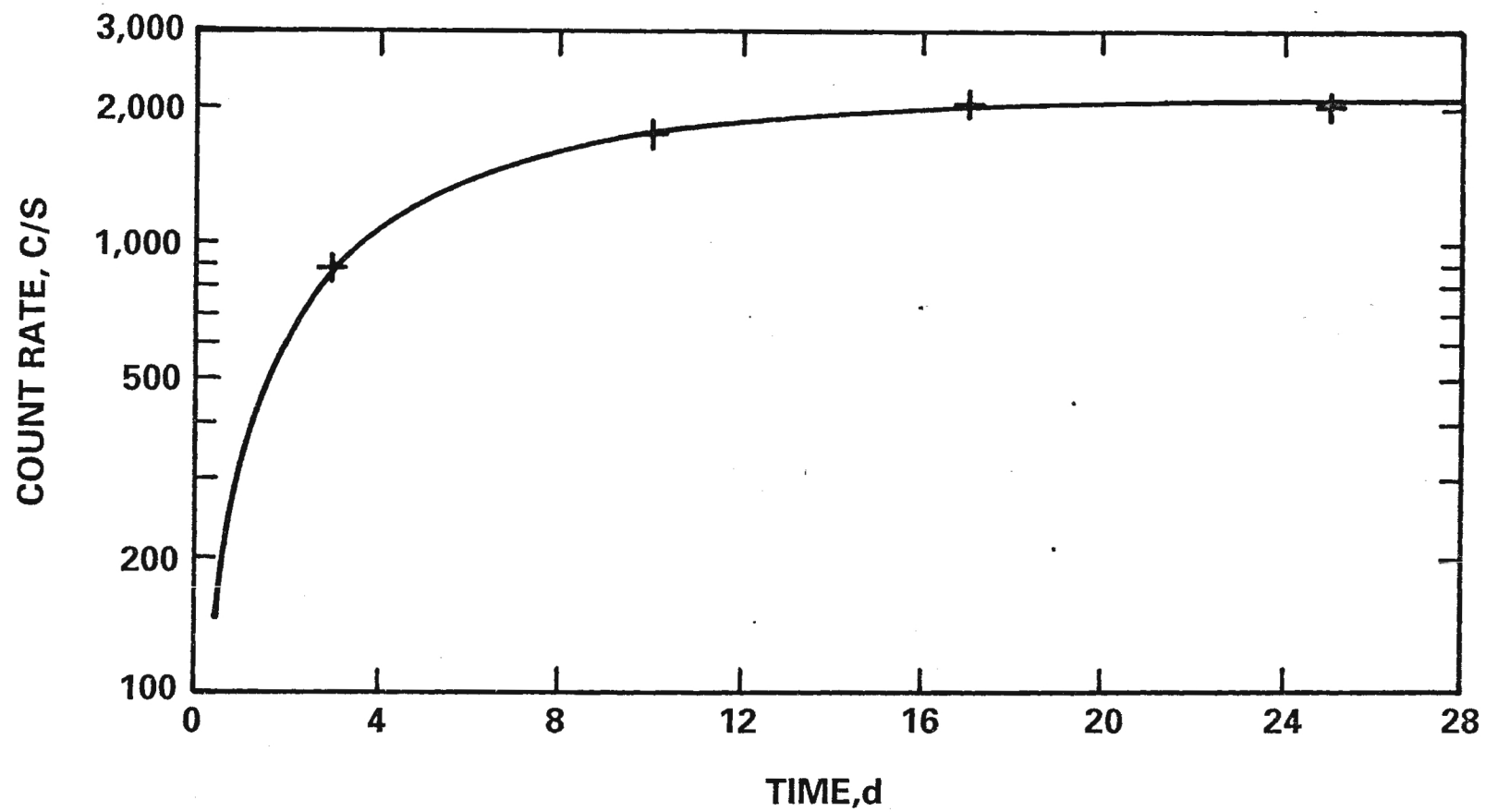


Figure 1. Calculated and measured ingrowth of radium-226 progeny

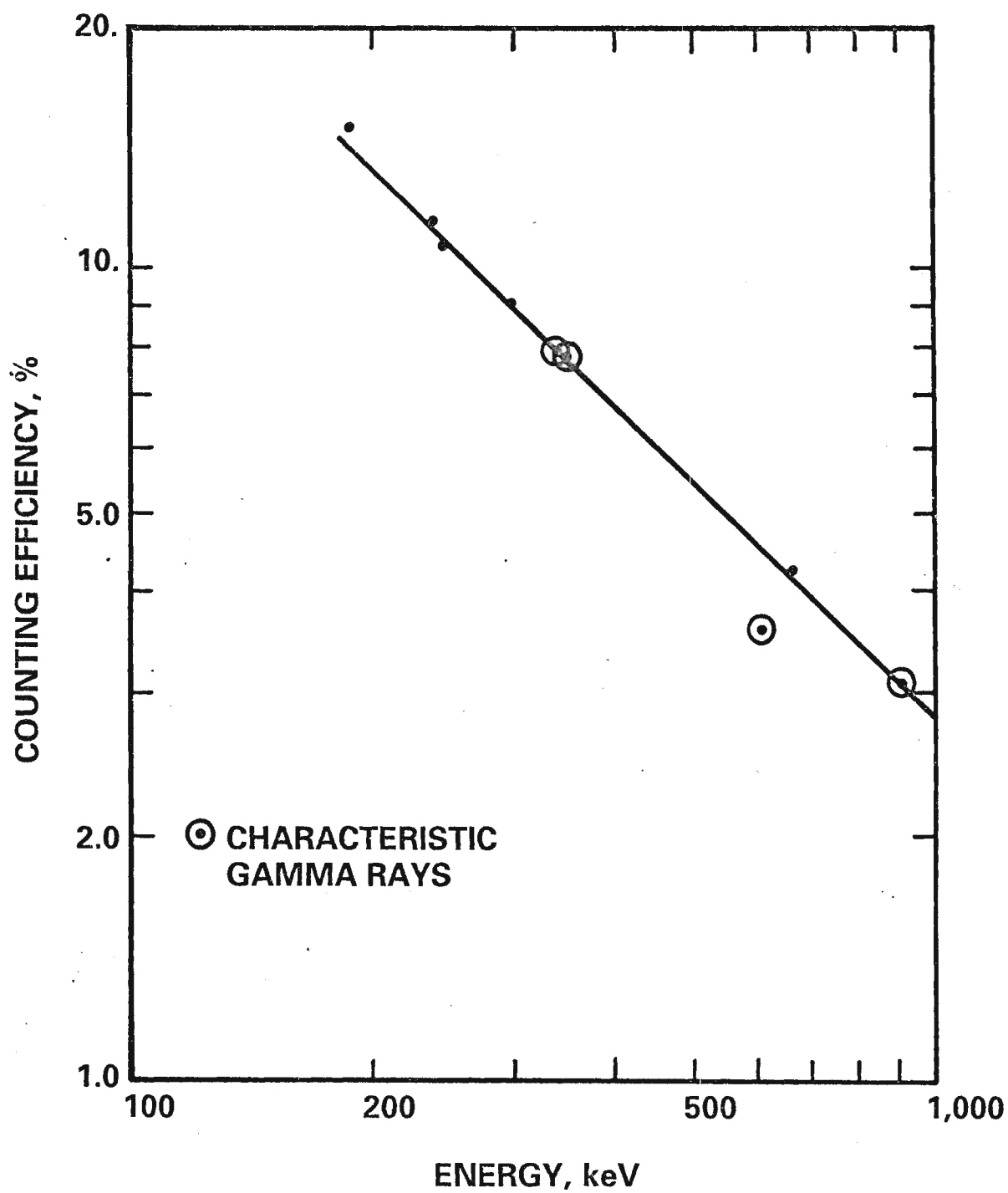


Figure 2. Counting efficiency as function of gamma-ray energy for samples on 47-mm dia. filter measured by Ge(Li) detector

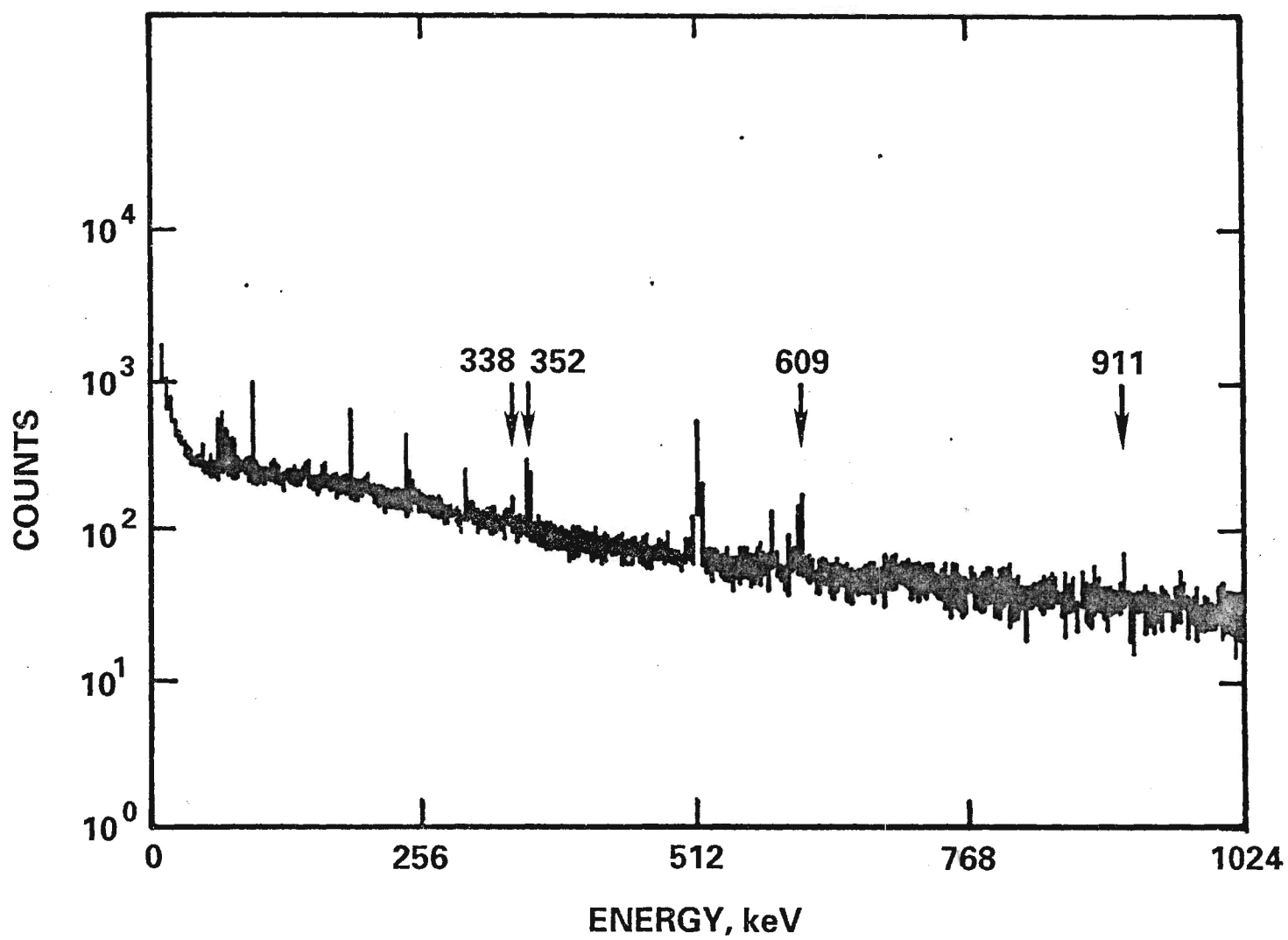


Figure 3. Detector background (200,000-s period)