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 1983

Final report: March 1989

Prepared for the

US Environmental Protection Agency

Assistance ID No. CR-813-630-01

Table of Contents

Tables

Figures

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.

4

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.

11

ANALYTICAL PROCEDURES

The 3.78-L sample is preserved by adding 60 ml 1 $\underline{N}$ nitric acid (Krieger and Whittaker 1980). To precipitate barium sulfate, the sample is further acidified with 20 ml concentrated (12 $\underline{N}$) hydrochloric acid; 5 ml barium carrier (88 mg $BaCl_2.2H_2O$) is pipetted into the solution and mixed with it; and 20 ml 18 $\underline{N}$ 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

18

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.

REFERENCES

Bivens, N. Radium-228 procedure, Columbia SC 29201: South Carolina Dept. of Health and Environmental Control, personal communication; 1986.

Blanchard, R.L.; Hahne, R.M.A.; Kahn, B.; McCurdy, D.; Mellor, R.A.; Moore, W.S.; Sedlet, J.; Whittaker, E. Radiological sampling and analytical methods for national interim primary drinking water regulations. Health Phys. 48: 587-600; 1985.

Brooks, I.B.; Blanchard, R.L. A procedure for the determination of radium-228. Montgomery AL 36109: U.S. Environmental Protection Agency, unpublished; 1980.

Cline, W.; Adamovitz, S.; Blackman, C.; Kahn, B. Radium and uranium concentrations in Georgia community water systems. Health Phys. 44: 1-12; 1983.

Godoy, J.M.; Schuettelkopf, H. Determination of radium-228 by counting Cerenkov radiation of actinium-228. Kernforschungszent. Karlsruhe Ber. KfK 3522; 1983.

Henry, J. Radium-228 analysis. Little Rock AR: Arkansas State Dept. of Health, personal communication; 1982.

Kirby, H.W.; Salutsky, M.L. The Radiochemistry of radium. Springfield VA 22151: National Technical Information Service. U.S. Atomic Energy Commission NAS-NS-3057; 1964.

Kloke, F.C.; Smith, E.T.; Kahn, B. The influence of radon daughter concentrations in air on gamma spectrometer

background. Nucl. Instr. Methods 34: 61-65; 1965.

Krieger, H.L.; Whittaker, E.L. Prescribed procedures for measurement of radioactivity in drinking water. Cincinnati, OH 45268; U.S. Environmental Protection Agency EPA-600/4-80-032; 1980.

Lieberman, R. Radiochemical determination of gross alpha activity in drinking water by precipitation. In: Eastern Environmental Radiation Facility radiochemistry procedures manual. Montgomery AL 36109: U.S. Environmental Protection Agency EPA-520/5-84-006; 1984,

Lucas, H.F. An improved method for the simultaneous determination of radium-224, -226 and -228 in water, soils and sediments. In: Radon in ground water, B. Graves ed. Chelsea Mich.: Lewis Publishers; 1987: 219-225.

Martin, M.J. Nuclear decay data for selected radionuclides. In: A handbook of radioactivity measurements procedures. Bethesda MD 20814: National Council on Radiation Protection and Measurements NCRP Report No. 58; 1985: 350-507.

McCurdy, D.E.; Mellor, R.A. Determination of radium-224, -226, and -228 by coincidence spectrometry. Anal Chem. 53: 2212-2216; 1981.

Michel, J.; King, P.T.; Moore, W.S. Gamma-ray spectrometry for determination of radium-226 and radium-228 in natural waters. Anal. Chem. 53: 1885-1889; 1981.

Noyce, J.R. Evaluation of methods for the assay of radium-228 in water. Washington DC 20234: National Bureau of Standards Technical Note 1137; 1981.

Percival, D.R.; Martin, D.B. Sequential determination of radium-226, radium-228, actinium-227 and thorium isotopes in environmental and process waste samples. Anal. Chem. 46:1742-1748; 1974.

U.S. Environmental Protection Agency. National interim primary drinking water regulations. Washington, D.C.: EPA-570/9-76-003; 1976.

Velten, R.J.; Jacobs, B.J. Determination of radium-228 in drinking water by liquid scintillation counting. Cincinnati OH 45268: U.S. Environmental Protection Agency Method 904.1, unpublished; 1983.

Weast, R.C. Handbook of chemistry and physics. 5th ed. Cleveland: CRC Press; 1978: B-232.

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
Radium-228 at equilibrium								
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
Radium-226 at equilibrium								
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 = (gross count +
              continuum + 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: $(2s.d.)^2$ combined = $(s.d.)_1{}^2 + (s.d.)_2{}^2$

         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	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	0.9	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, $\underline{N}$	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. 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±0.3	7.9
Ac-228	911.1	26.6±0.7	3.1
Pb-214	351.9	35.4±0.3	7.8
Bi-214	609.3	44.8±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 ommitted 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		detector		2 S.D. for 1 pCi/L, pCi/L
		cont. from 1 pCi/L Ra-228	cont. from 1 pCi/L Ra-226	cont.	peak	
Radium-228 at equilibrium						
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
Radium-226 at equilibrium						
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

Activity added, pCi/L		Activity measured, pCi/L	
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

| Radium-228, pCi/L | | Radium-226, pCi/L | |
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
		7.1		11.4
		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
		9.5		15.3
		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
		9.2		5.4
		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	Radium-226, pCi/L		Radium-228, pCi/L	
		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
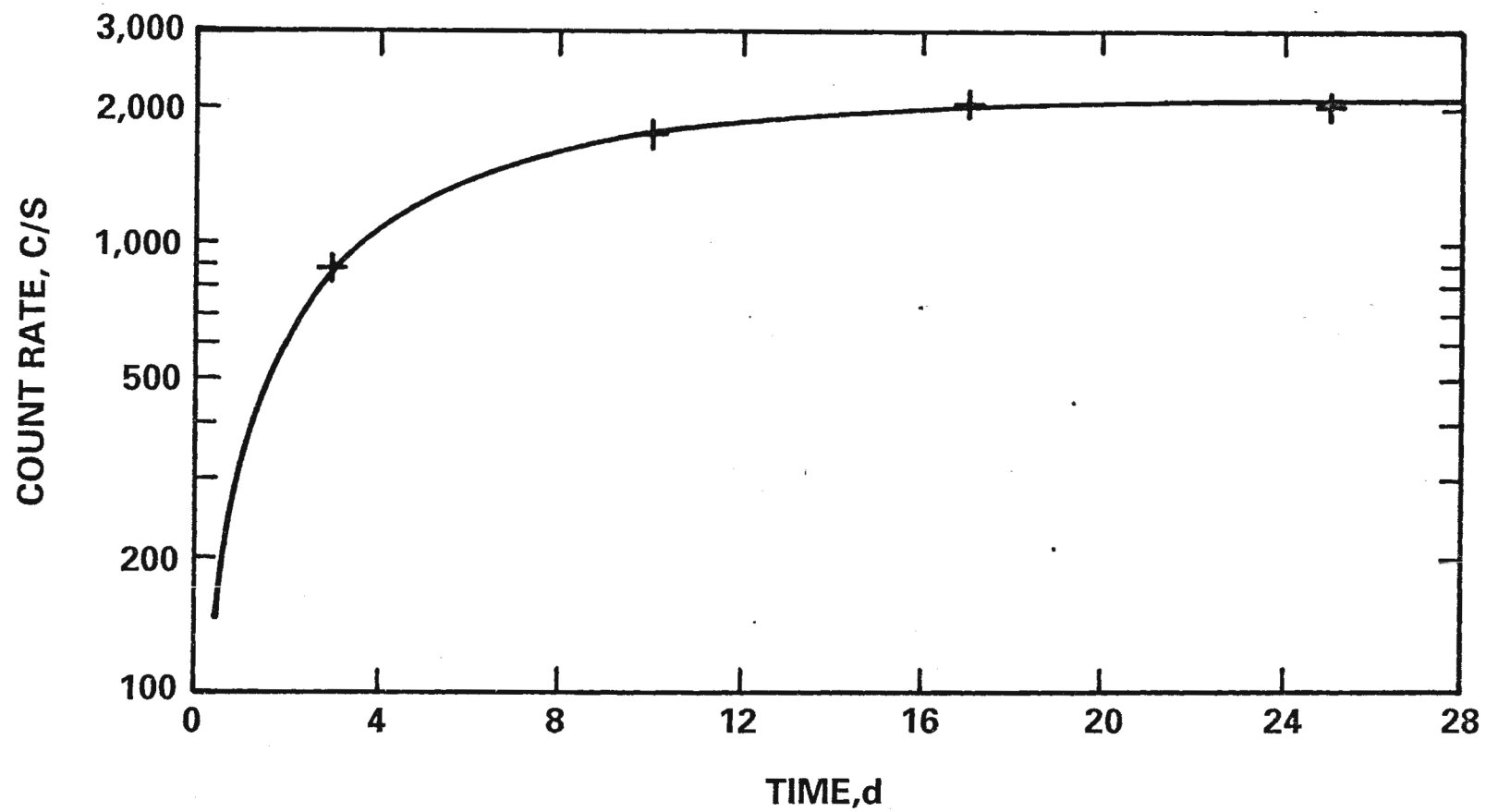   2. Plus/minus values are 2 standard deviations of counting.

Figure 1. Calculated and measured ingrowth of radium-226 progeny
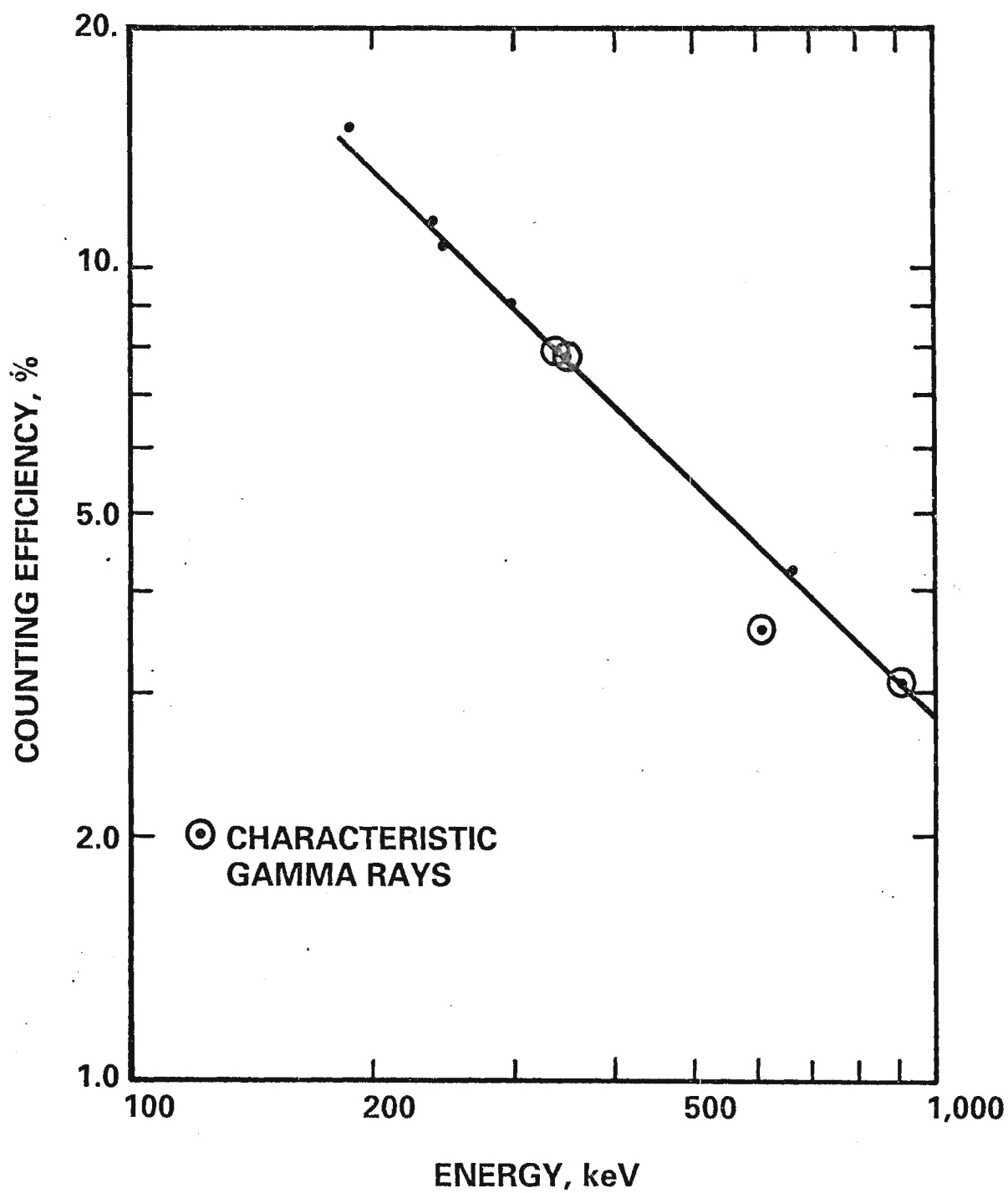
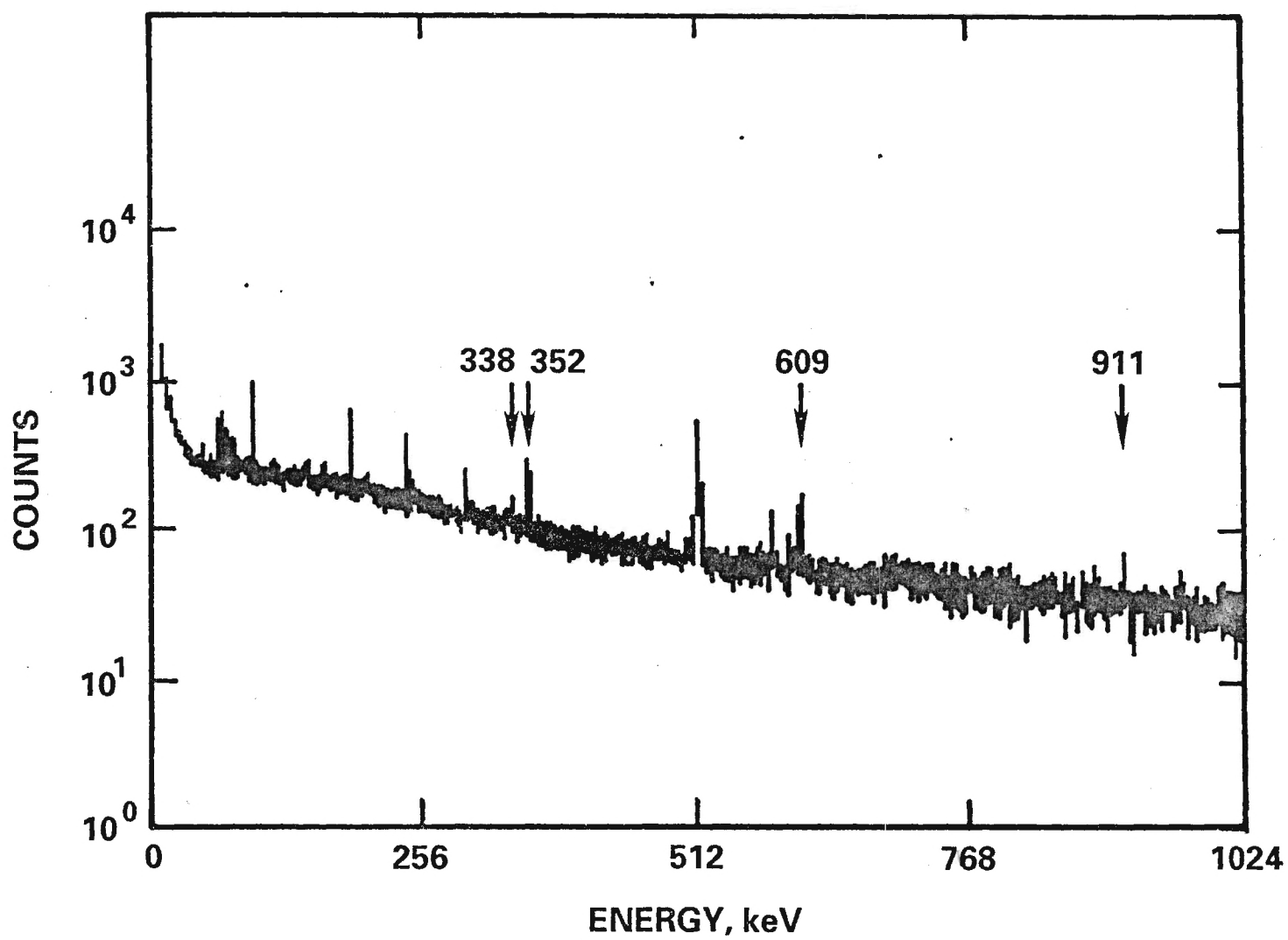Figure 2. Counting efficiency as function of gamma-ray energy for samples on 47-mm dia. filter measured by Ge(Li) detector

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