# DETERMINATION OF RADIUM-226 AND RADIUM-228 IN WATER, SOIL, AIR AND BIOLOGICAL TISSUE

## 1. Principle

1.1 A sequential method for the determination of radium-226 and radium228 is described.

1.2 Radium is precipitated with barium sulfate. Barium-radium-sulfate is dissolved in a pentasodium diethylenetriaminepentaacetate solution and transferred to an emanation tube and the radon allowed to come to equilibrium, approximately 30 days. Radium-226 ($T_{½}$ = 1602 years) decays by alpha emission to radon-222. Radon-222 ($T_{½}$ = 3.825 days), a noble gas, is separated and collected from the liquid by a de-e-Anation technique. The radon-222 is counted by alpha scintillation 4 ½ hours after de-emanation, at which time the short-lived progeny have reached 97+% of equilibrium.

1.3 The radium solution from the radium-226 determination is saved and the radium is reprecipitated. Radium-228 ($T_{½}$ 6.1 years) is a beta emitter and decays to actinium-228 ($T_{½}$ 6.13 hours). The actinium is allowed to ingrow for 3 days and is extracted with 2-di-ethylhexylphosphoric acid and back-extracted with nitric acid. The actinium-228 is beta-counted in a low level proportional counter.

## 2. Application

2.1 This method is applicable for the determination of radium-226 and radium-228 in water, soil, air, biological tissues, and biological fluids.

3. No range has been determined; however, samples that contain 100 nCi of radium-226 have been analyzed.

## 4. Interferences

4.1 Radium-223 ($T_{½}$ = 11.43 days) and radon-219 ($T_{½}$ = 3.92 seconds) will interfere in samples of fresh uranium mill effluents. This interference in water and soil samples is small and may be eliminated in mill effluents by allowing the radon-219 to decay and transferring the radon-222 to a separate scintillation detector and recounting.

## 5. Lower limit of detection

5.1 The lower limit of detection* (LLD) is defined as the smallest concentration of radioactive material sampled that has a 95% probability of being validly detected.

$$LLD = \frac{4.66\ S_b}{2.22 \times E \times S}$$

* HASL Procedures Manual, J. H. Harley, editor, pages D-08-01/12, August 1977.

where 4.66 = $2\sqrt{2}$ k, where k is the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present ($\propto$) = .05

$S_b$ = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

The expected precision for radium-226, based on the 95% confidence level analytical error, is 0.3 pCi/liter for samples up to 1.0 pCi/ liter and 30% for samples above 1.0 pCi/liter. These are the values used in the Duplicate Analysis Program and are recommended by the Quality Assurance Branch.

Over a period of 2 years, 9 cross-check samples containing known amounts of radium-226 were received from the Quality Assurance Branch. None of these results were outside the 3-sigma control limits.

7. Shipment and storage of samples and sample stability

7.1 Water: The water sample must be adjusted to pH 1 with nitric acid. If suspended solids are present and separate analyses are required for the suspended and dissolved solids, the sample must be filtered in the field and the water adjusted to pH 1 with nitric acid. Water samples after pH adjustment may be preserved for 6 months.

7.2 Urine: The sample should represent a 24-hour composite.

7.3 No special precautions are necessary for other sample types.

8. Reagents

8.1 Acetic acid, concentrated: Reagent grade.

8.2 Acetic acid, 6N: Add 345 ml reagent grade glacial acetic acid to 500 ml distilled water and dilute to 1000 ml.

8.3 Actinium wash solution: Dissolve 100 g reagent grade monochloroacetic acid, 2.4 ml of 41% pentasodium diethylenetriaminepentaacetate ($Na_5$DTPA), 25.4 g sodium hydroxide in 800 ml distilled water and dilute to 1000 ml.

8.4 Air, aged: Commercial grade compressed air. Store for at least 6 months before use.

8.5 Barium carrier, 10 mg/ml: Dissolve 19.0 g reagent grade barium nitrate in 800 ml distilled water and dilute to 1000 ml.

8.6 Barium carrier, 5 mg/ml: Dissolve 4.75 g barium nitrate in 400 ml distilled water and dilute to 500 ml.

8.7 Pentasodium diethylenetriaminepentaacetate ($Na_5$DTPA) reagent grade, 0.17M: Add 400 ml of distilled water to 209 ml 41% solution DTPA. Filter through glass fiber wool with suction. Dilute to 1000 ml with distilled water. Adjust to pH 12 with perchloric acid or sodium hydroxide.

8.8 2-di-ethylhexylphosphoric acid (HDEHP), 15% in n-heptane: Dilute 150 ml HDEHP to 1000 ml with n-heptane. Transfer to a 2-liter separatory funnel. Wash twice with 200 ml of a one-to-one mixture 2M diammonium citrate and concentrated ammonium hydroxide, and twice with 200 ml 4N nitric acid.

8.9 Hydrofluoric acid, 48%: Reagent grade.

8.10 Hydrochloric acid, concentrated: Reagent grade.

8.11 Hydrochloric acid, 4N: Add 333 ml concentrated hydrochloric acid to 600 ml distilled water. Cool and dilute to 1000 ml.

8.12 Hydrochloric acid, 2N: Add 167 ml concentrated hydrochloric acid to 600 ml distilled water. Cool and dilute to 1000 ml.

8.13 Hydrogen peroxide, 30%: Reagent grade.

8.14 Lead carrier, 100 mg/ml: Dissolve 165.6 g reagent grade lead nitrate in 800 ml distilled water and dilute to 1000 ml.

8.15 Monochloroacetic acid, 2M: Dissolve 189 g reagent grade monochloroacetic acid in 1000 ml distilled water.

8.16 Nicholson's Flux: In a 500-ml platinum dish, add 65.8 g potassium carbonate, 50.5 g sodium carbonate, 33.7 g sodium tetraborate-decohydrate and 30 mg barium sulfate. Mix and fuse. Cool and grind to pass a 10-mesh screen.

8.17 Nitric acid, concentrated (70%): Reagent grade.

8.18 Nitric acid, N: Add 63 ml concentrated nitric acid to 600 ml distilled water. Cool and dilute to 1000 ml.

8.19 Phosphoric acid, concentrated: Reagent grade.

8.20 Sodium sulfate, 20%: Dissolve 20 g anhydrous sodium sulfate in 80 ml distilled water and dilute to 100 ml.

8.21 Sodium sulfate 2.5%: Dissolve 2.5 g anhydrous sodium sulfate in 80 ml distilled water, add 1 ml concentrated sulfuric acid, dilute to 100 ml with distilled water.

8.22 Sulfuric acid, concentrated: Reagent grade.

9. Apparatus

9.1 Low background beta counter.

9.2 Parr acid digestion bomb.

9.3 Radon bubbler (Figure 5).

9.4 Radon transfer apparatus (Figure 6).

9.5 Scintillation cell (Figure 7).

10. Procedure

WATER

10.1 Transfer 1500-ml sample to a 2-liter beaker. Adjust pH to approximately 1.0 with concentrated nitric acid and add 200 mg lead carrier.

10.2 Add 100 ml concentrated sulfuric acid and heat at 70°C with stirring for 1 hour. Allow the lead sulfate to settle overnight. Decant, discard the supernate, and transfer precipitate to a 40-ml centrifuge tube using distilled water. Centrifuge, and discard the supernate.

10.3 Add 1 ml concentrated acetic acid, 6 ml 41% $Na_5$DTPA and 1 ml distilled water. Add stir bar and heat with stirring until dissolution is complete.

10.4 Transfer the solution to radon bubbler (Figure 1). Do not exceed 9 ml total volume. Seal bubbler with Pyseal cement and allow the radon to ingrow. De-emanate as in section 10-46.

SOIL, MILL TAILINGS AND ORES

10.5 Weigh, in a porcelain crucible, a suitable portion of sample & not over 1 gram) on an analytical balance. Heat overnight at 600°C. Cool.

10.6 Add 7 ml 48% hydrofluoric acid to the Parr acid digestion bomb and thenlzlawly transfer the sample into the acid. Seal bomb and heat in an oven at 150°C for 2 to 3 hours, cool. (Caution: Never allow temperature to exceed 150°C and use sufficient care in opening bomb).

10.7 Transfer to 50-ml platinum dish using minimum distilled water and add 5 ml concentrated nitric acid. Evaporate to dryness and cool.

10.8 Add 5 ml 48% hydrofluoric acid and 5 ml concentrated nitric acid and again evaporate to dryness and cool.

10.9 Add 4 ml concentrated sulfuric acid, dropwise to rinse the sides of the dish. Place the dish on a hot plate, swirl the dish to slow reaction, if needed. Add remainder of the sulfuric acid.

10.10 Add 2 g anhydrous sodium sulfate, heat dish on hot plate until liquid has evaporated. Heat dish carefully over a low flame, swirling melt to facilitate dissolution of sample. Do not heat after clear fusion has been obtained.

10.11 Transfer the dish and cake to a 400-ml beaker, containing 100 ml distilled water. Add, with caution, 30 ml concentrated hydrochloric acid and 30 ml concentrated sulfuric acid. Remove dish, rinse with distilled water, and save for step 10.15 in this procedure. Heat, with stirring, until cake has dissolved.

10.12 Add 5 ml of 10-mg/ml barium carrier. Add the carrier dropwise, letting the first drop become well mixed before adding the next drop. Repeat this until 4 or 5 drops have been added, then add the rest of the carrier.

10.13 Cover with watch glass and bring to a boil. Cool and add 5 ml 30% hydrogen peroxide. Allow to settle overnight.

10.14 Filter through a Millipore filter, type HA 0.45 micron. Wash beaker and precipitate with 2.5% sodium sulfate in 1% sulfuric acid. Discard filtrate. Save 400-ml beaker for step 10.18 of this procedure.

10.15 Place filter in 50-ml platinum dish. Ash and cool.

10.16 Add 4 g Nicholson flux. Heat over a blast burner until the melt is clear. Cool.

10.17 Place dish and cake in 400-ml beaker (saved from 10.11) containing 100 ml distilled water. Add 20 ml concentrated sulfuric acid. After cake has dissolved, remove dish, rinsing with distilled water. (Save for step 10.20 of this procedure). Cover and let set overnight.

10.18 Filter through a Millipore filter, type HA 0.45 micron. Wash beaker and precipitate with 2.5% sodium sulfate in 1% sulfuric acid. Discard filtrate.

10.19 Place filter in 50-ml platinum dish. Ash and cool.

10.20 Add 1 ml concentrated phosphoric acid, carefully heat and swirl until a clear solution is obtained. Cool.

10.21 Dissolve, with heat, the barium phosphate in 40 ml of 4N hydrochloric acid and evaporate to 2 ml. Add 5 ml 2N hydrochloric acid with heat and transfer to radon bubbler. Do not exceed 9 ml. Seal bubbler with Pyseal cement and allow the radon to ingrow and collect. De-emanate as indicated in section 10.43.

GLASS-FIBER AIR FILTERS

The unused filters are weighed on an analytical balance and the tare is recorded on the glassine envelope.

10.22 Reweigh the used filter or filters. Transfer to a 400-ml Teflon beaker. (If polonium-210 is requested, add polonium-208 tracer).

10.23 Add 30 ml concentrated hydrofluoric acid and 30 ml concentrated nitric acid. Heat at reflux for several days, adding more acid as necessary until a white solution and precipitate is obtained.

10.24 Add 30 ml concentrated hydrochloric acid and heat to dryness. Repeat two more times.

If uranium, thorium, or polonium analyses are requested, dissolve residue in 6N hydrochloric acid and transfer to a 100-ml volumetric flask and dilute to mark with 6N hydrochloric acid. Mix by shaking. Transfer 50 ml for radium analysis to a 250-ml beaker. Continue at 10.25.

10.25 Add with stirring, 5 ml of 10 mg/ml barium carrier and 20 ml concentrated sulfuric acid. Cool and let set overnight.

10.26 Cover with watch glass and bring to a boil. Cool and add 5 ml 30% hydrogen peroxide. Allow to settle overnight.

10.27 Filter through a Millipore filter, type HA 0.45 micron. Wash beaker and precipitate with 2.5% sodium sulfate in 1% sulfuric acid. Discard filtrate. Save 400-ml beaker for step 10.18 of this procedure.

10.28 Place filter in 50-ml platinum dish. Ash and cool.

10.29 Add 4 g Nicholson's flux. Heat over a blast burner until the melt is clear. Cool.

10.30 Place dish and cake in 400-ml beaker (saved from 10.11) containing 100 ml distilled water. Add 20 ml concentrated sulfuric acid. After cake-has dissolved, remove dish, rinsing with distilled water. (Save for step 10.20 of this procedure). Cover and let set overnight.

10.31 Filter through a Millipore filter, type HA, 0.45 micron. Wash beaker and precipitate with 2.5% sodium sulfate in 1% sulfuric acid. Discard filtrate.

10.32 Place filter in 50-ml platinum dish. Ash and cool.

10.33 Add 1 ml concentrated phosphoric acid, carefully heat and swirl until a clear solution is obtained. Cool.

10.34 Dissolve, with heat, the barium phosphate in 40 ml of 4N hydrochloric acid and evaporate to 2 ml. Add 5 ml 2N hydrochloric acid with heat and transfer to radon bubbler. Do not exceed 9 ml. Seal bubbler with Pyseal cement and allow the radon to ingrow and collect. De-emanate as indicated in section 10.43.

AIR FILTER, MICROSORBAN

10.35 Place weighed filter in a 1000-ml Pyrex beaker. (Add polonium and uranium tracers if sample is to be split for polonium and uranium analysis). Add 25 ml concentrated sulfuric acid to a 1-to-4 filter composite (40 ml of acid if a larger composite or 20 cm x 25 cm (8”x 10”) filter is to be analyzed).

10.36 Heat on a hot plate with high heat until dense white fumes are visible. Remove from hot plate and carefully wash the sides of the beaker with 30% hydrogen peroxide and concentrated

nitric acid. Reheat to fumes. Repeat the hydrogen peroxide and nitric acid until all organic material is gone.

10.37 Evaporate to approximately 10 ml, cool and transfer to a 250-ml Teflon beaker. Rinse well with distilled water. Add 30 ml hydrofluoric acid and 30 ml concentrated nitric acid. Cover and digest overnight with medium heat.

10.38 Heat to dense white fumes to remove the hydrofluoric and nitric acid.
Cool and transfer to a 100-ml volumetric flask with distilled water. Dilute to 100 ml.

10.39 Transfer a 50-ml aliquot to a 250-ml beaker. Add 1 ml of 5-mg/ml lead carrier dropwise with stirring. Let set overnight.

10.40 Decant, discard the supernate, and transfer to a 40-ml centrifuge tube using distilled water. Centrifuge, and discard the supernate.

10.41 Add 1 ml concentrated acetic acid, 6 ml Na5DTPA and 1 ml distilled water. Add stir bar and heat with stirring until dissolution is complete.

10.42 Transfer the solution to radon bubbler (Figure 5). Do not exceed 9-mi total volume. Seal bubbler with Pyseal cement and allow the radon to ingrow. De-emanate as in section 10-44.

RADON DE-EMANATION

Figure 6 illustrates the assembled apparatus.

10.43 Attach a scintillation chamber to the manometer. Attach the radon bubbler containing the sample to an Ascarite-Drierite drying tube and a short length of thermometer tubing with short lengths of gum rubber tubing.

10.44 Open stopcock A and apply vacuum to system. When the right-hand leg of the U-tube manometer has reached its maximum height, close stopcock A. The system should be left in this configuration for 3 to 5 minutes. If the mercury begins to drop in the right-hand leg, check the glass joints and rubber tubing connections for leaks. Apply a very light coating of Dow-Corning Silicone grease to connection if necessary, then repeat system integrity check.

10.45 Open stopcock A and B and permit the mercury in the right-hand leg of manometer to reach its maximum height. Close stopcock A and check for leaks as in 10.32.

10.46 Connect dry aged air with gum rubber tubing to the radon bubbler. The air pressure should be limited to two psi.

10.47 Start de-emanation by opening stopcock C slowly to prevent pressure surge. After bubbling has ceased, open stopcock D slowly. Adjust flow of aged air. Thirty minutes is required to complete the de-emanation.

10.48 When mercury in both legs of the manometer is equal, shut stopcocks D, C, and B in that order.

10.49 Remove the scintillation chamber and place in light-tight counting cabinet for the 4-1/2-hour ingrowth period.

10.50 Remove the purged bubbler and save for the radium-228 determination.

RADIUM-228 DETERMINATION

10.51 After radon de-emanation, transfer the sample from the radon bubbler to a 40-ml centrifuge tube. Wash bubbler with 4N hydrochloric acid and force through glass frit with suction. Add with stirring 2 ml concentrated sulfuric acid and 1 ml 20% sodium sulfate. Digest 5 to 10 minutes in hot water bath, cool and centrifuge.

10.52 Decant supernate and save precipitate.

10.53 Add 15 ml of 0.17M DTPA to the precipitate. Place in boiling water bath and heat with stirring for 10 minutes to dissolve the precipitate. (If lead was used as radium carrier, 10 mg $Ba^{2+}$ must be added as radium carrier.) Add 1 ml 20% sodium sulfate solution and enough water to bring solution to 28 ml. Add 2 ml 6M acetic acid. Continue to heat in bath with stirring for 5 minutes. Cool for 5 minutes in ice water bath. Centrifuge and discard supernate.

10.54 Add 15 ml 0.17M DTPA and stir bar to the precipitate. Place in boiling water bath and heat with stirring until the precipitate has dissolved. Add 1 ml 20% sodium sulfate solution. Add water to bring volume to 28 ml. Add 2 ml 6M acetic acid. Record time $T_1$ when 2 ml 6M acetic acid is added. ($T_1$ time is start of ingrowth of actinium-228.) Continue to heat in boiling water with stirring for 5 minutes. Cool for 5 minutes in ice water. Add 4 drops 2.5-mg/ml barium carrier with stirring, with 5-second intervals between drops. Cool for another 10 minutes, then centrifuge, discard the supernate.

10.55 Add 5 ml water to 40-ml centrifuge tube containing the barium sulfate and allow at least 30 hours ingrowth of 6.13-hour actinium-228.

10.56 At the end of the ingrowth period, dissolve the barium sulfate in 15 ml 0.17M DTPA. Add 1 ml 20% sodium sulfate, dilute to 28 ml with water, and reprecipitate the barium sulfate with 2 ml 6N acetic acid. Record time of this precipitation as $T_2$. Digest in boiling water bath for 5 minutes. Cool in ice bath.

10.57 Centrifuge and decant the supernate into a clean 40-ml centrifuge tube. Before returning tube upright, rinse walls very carefully with 2 to 3 ml of water. Do not disturb the precipitate. Add wash solution to the clean 40-ml centrifuge tube.

10.58 Add 1 ml 5-mg/ml barium carrier to the centrifuge tube containing the supernate. Stir. Place in boiling water bath, heat with stirring for 5 minutes. Cool in ice water bath for 5 minutes. Centrifuge.

10.59 Decant the supernate into 125-ml separatory funnel containing 5 ml 2M monochloroacetic acid. Discard the barium sulfate precipitate.

10.60 Add 10 ml washed 15% HDEHP in n-heptane to the 125-ml separatory funnel. Shake vigorously for 2 minutes (relieve pressure as needed) and discard the aqueous phase.

10.61 Wash organic phase for 1 minute with two 10-ml portions of actinium wash solution. Discard the aqueous phases.

10.62 Add 10 ml 1N nitric acid, mix phases for I minute, draw off aqueous phase into 2-inch planchet. Evaporate to dryness.

10.63 Repeat step 10.62 using 5 ml 1N nitric acid, discard organic phase.

10.64 Continue heating the planchet until all possible nitric acid vapor has been removed, cool.

10.65 Place in low-background beta counter and count for 50 minutes. Record count time, $T_3$, as end of actinium-228 decay.

11. Calibration

Known amounts of radium-226 are added to the various sample types and these samples are then analyzed in accordance with the various procedures.

11.1 Reagents

11.1.1 Dilute a National Bureau of Standards radium-226 standard to 100 pCi/liter using distilled water. Adjust pH to 1 with concentrated nitric acid.

RADIUM-226

11.2 Procedure

11.2.1 Add 1 ml of the 100-pCi/ml radium-226 standard to appropriate sample size for the sample type and proceed with the method for that sample.

11.2.2 After counting the radon, use the following equation, which includes ingrowth, decay, counting efficiency, de-emanation efficiency, and chemical yield, to determine scintillation cell factor.

$$\text{Cell factor} = \frac{\text{cpm at equilibrium}}{\text{pCi of standard}}$$

Scintillation cells should be numbered and a record kept of the individual cell factors.

RADIUM-228

None of the suppliers of radionuclide standards distribute a radium-228 standard. A thorium-232 standard supplied by Amersham is being used for standardization. This standard was prepared in 1906 and the radium-228 has ingrown to equilibrium.

11.2.3 Weight 0.100 9 of the thorium-232 standard. Dissolve and dilute to 100 ml with distilled water.

11.2.4 Pipet 10 ml of the dilute standard to a 40-ml centrifuge tube. Add 10 mg barium carrier and 2 ml concentrated sulfuric acid. Digest 5 to 10 minutes in a hot water bath. Cool and centrifuge.

11.2.5 Decant supernate and save precipitate. Proceed as indicated in the radium-228 determination, Section 10.40.

11.2.6 Use data obtained to determine combined yield and counting efficiency.

$$\text{Yield and counting efficiency} = \frac{\text{cpm}}{\text{dpm}}$$

where cpm = counts per minutes obtained on weightless planchet
dpm = disintegrations per minute calculated from thorium-232 concentration in standard

12. Quality Control

Every tenth sample is recycled as a blind duplicate. The results of the duplicates are subject to standard statistical tests and results outside the control limits are examined for possible remedial action.

Standard samples are received from the Quality Assurance Branch. If the results are unsatisfactory, the reason for the problem is found and all results during the questionable time are evaluated for possible remedial action.

13. Calculation

13.1 Radium-226

$$\text{Radium-226 (pCi/liter or g)} = \frac{A}{F \times S}$$

where A = net counts per minute
F = cell factor (as determined in 11.2.2)
S = sample size, liters or grams

13.2 Radium-228

$$\text{Radium-228 (pCi/liter or g)} = \frac{A}{2.22 \times EY \times (1-e^{-\lambda t1}) \times (e^{-\lambda t2}) \times V}$$

where A = net counts per minute
2.22 = disintegration per minute/pCi
EY = combined fractional counting efficiency and chemical yield

| | | |
|---|---|---|
| $t_1$ | = | T2 - T1 (ingrowth of actinium-228) (hours) |
| $t_2$ | | T3 - T2 (decay of actinium-228) (hours) |
| $\lambda$ | = | $1n2/T_{1/2}$ = 0.113 (hours) |
| V | = | sample size (liter or gram) |

14. References

Johns, F. B. "Handbook of Radiochemical Methods." EPA-680/4-75-001. February, 1975.

Percival, D. R. and D. B. Martin. "Analytical Chemistry 46." 1974.

Sill, C. W. and C. P. Willis. "Analytical Chemistry 37." 1965.

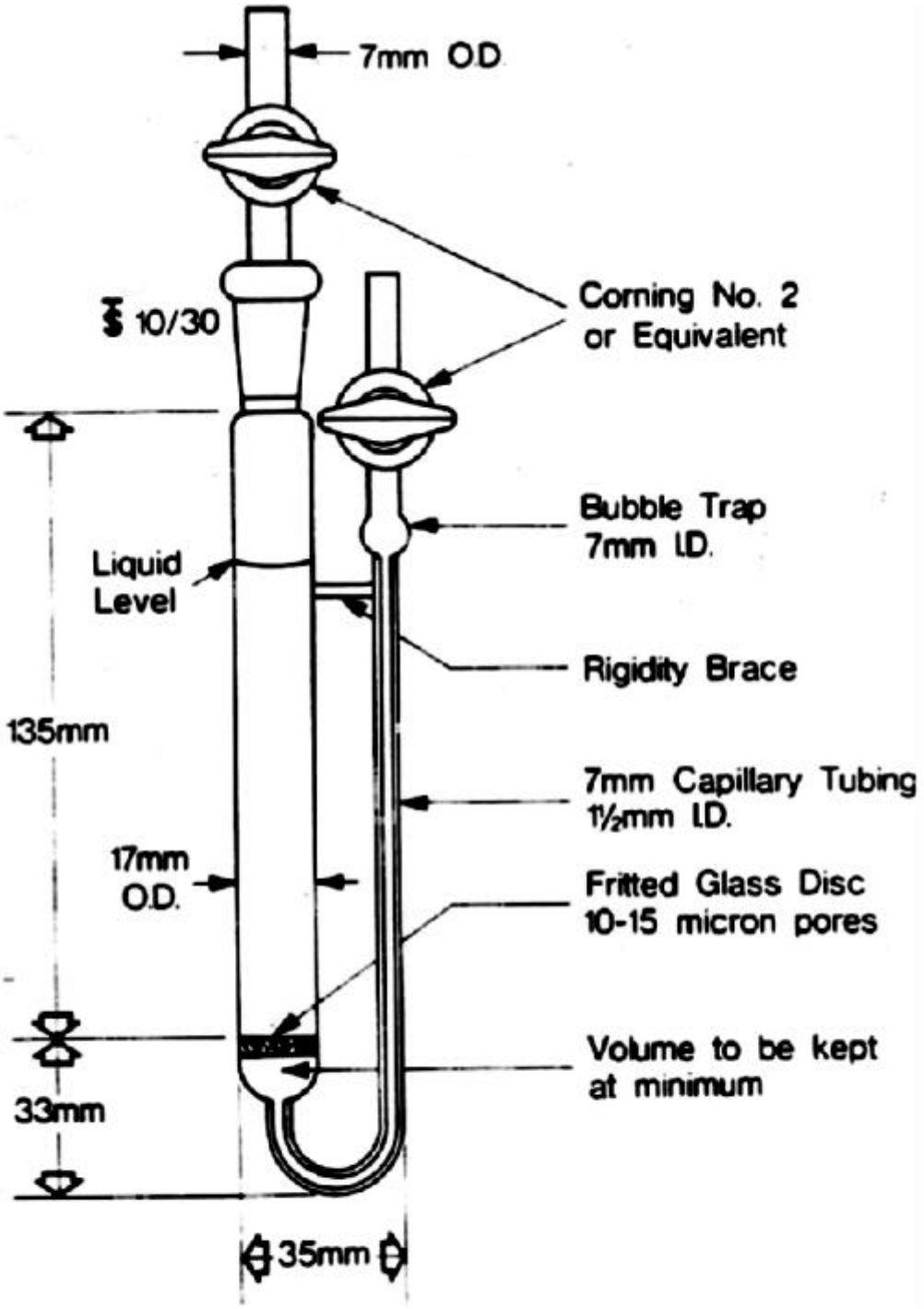


Figure 5. Radon Bubbler.

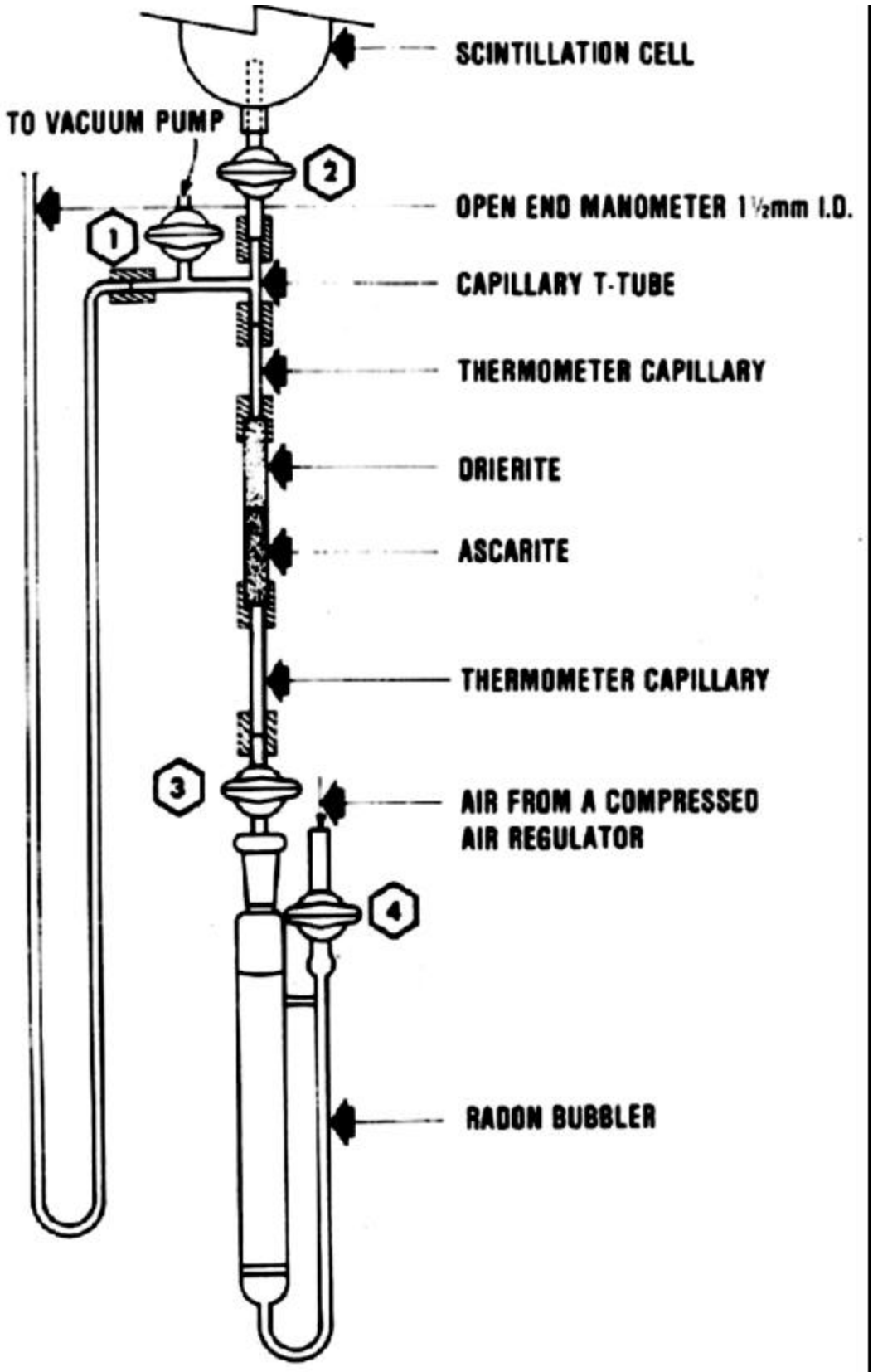


Figure 6. Radon Emanation Apparatus.

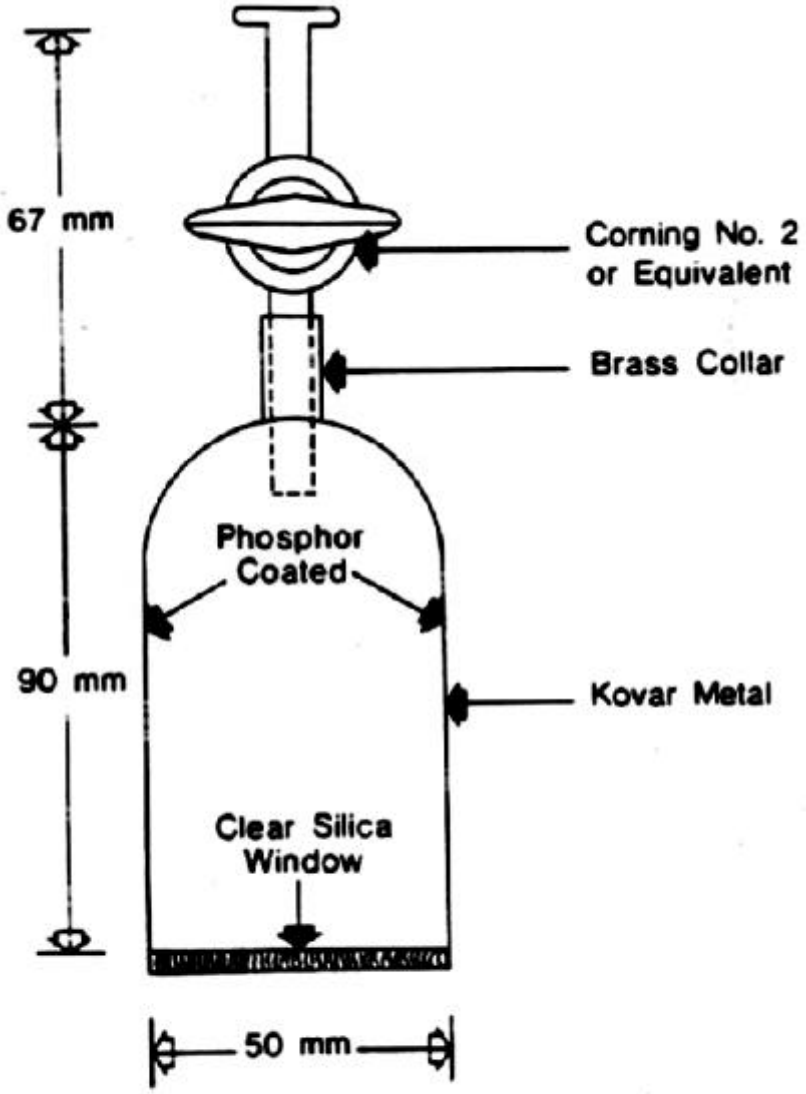


Figure 7. Lucas Scintillation Cell.