



Designation: D3454 – 21

Standard Test Method for Radium-226 in Water ¹

This standard is issued under the fixed designation D3454; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of soluble, suspended, and total ^{226}Ra in water in concentrations above 3.7×10^{-3} Bq/L. This test method is not applicable to the measurement of other radium isotopes.

1.2 This test method may be used for quantitative measurements by calibrating with a ^{226}Ra standard, or for relative measurements by comparing the measurements made with each other.

1.3 This test method does not meet the current requirements of Practice [D2777](#).

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.5 Hydrofluoric acid (HF) is very hazardous and should be used in a well-ventilated hood. Wear rubber gloves, safety glasses or goggles, and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills promptly and wash thoroughly after using HF.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.04](#) on Methods of Radiochemical Analysis.

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2. Referenced Documents

2.1 *ASTM Standards:*²

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3370 Practices for Sampling Water from Flowing Process Streams](#)

[D3649 Practice for High-Resolution Gamma-Ray Spectrometry of Water](#)

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

[D7902 Terminology for Radiochemical Analyses](#)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminologies [D1129](#) and [D7902](#).

4. Summary of Test Method

4.1 This test method is based on the emanation and scintillation counting of ^{222}Rn , a gaseous decay product of ^{226}Ra , from a solution.

4.2 ^{226}Ra is collected from water by coprecipitation on a relatively large amount of barium sulfate. The barium-radium sulfate is decomposed by fuming with phosphoric acid, and the resulting glassy melt is dissolved by evaporation with dilute hydrochloric acid to form soluble barium-radium phosphates and chlorides. These salts are dissolved, and the solution is stored for ingrowth of ^{222}Rn . After a suitable ingrowth period, the radon gas is removed from the solution by purging with gas and transferred to a scintillation counting chamber. About 4 h after ^{222}Rn collection, the scintillation chamber is counted for alpha activity. The ^{226}Ra concentration is calculated from the

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

alpha count rate of ^{222}Rn and its immediate progeny. The radioactive decay characteristics of ^{226}Ra and its immediate decay progeny are listed in Table 1.

5. Significance and Use

5.1 The most prevalent of the five radium isotopes in ground water, having a half life greater than one day, are ^{226}Ra and ^{228}Ra . These two isotopes also present the greatest health risk compared to the other naturally occurring nuclides of equal concentrations if ingested via the water pathway.

5.2 Although primarily utilized on a water medium, this technique may be applicable for the measurement of the ^{226}Ra content of any medium once the medium has been completely decomposed and put into an aqueous solution.

5.3 This test method is based on a method previously published by Rushing, et al. (1).³ The general methodology and basis of the technique are similar to that of Ref (2).

6. Interferences

6.1 Only the gaseous alpha-emitting radionuclides interfere, namely, ^{219}Rn and ^{220}Rn . Their half-lives are 3.98 s and 55.8 s, respectively; their presence indicates the presence of their parents, ^{223}Ra and ^{224}Ra . These short-lived radon isotopes decay before the ^{222}Rn is counted; it is their alpha-emitting decay products that would interfere. These interferences are very rare in water samples but are frequently observed in certain uranium mill effluents.

7. Apparatus

7.1 *Radon Bubbler* (Fig. 1).

7.2 *Radon Scintillation Chamber* (also known as Lucas Cell) (Fig. 2).

7.3 *Manometer*, open-end capillary tube or vacuum gage having a volume which is small compared to the volume of the scintillation chamber, 0 – 101 kPa (0 – 760 mmHg) (Fig. 3).

7.4 *Gas Purification Tube*, 7 to 8-mm outside diameter standard wall glass tubing, 100 mm long, constricted at lower end to hold a glass wool plug (Fig. 3). The upper half of the

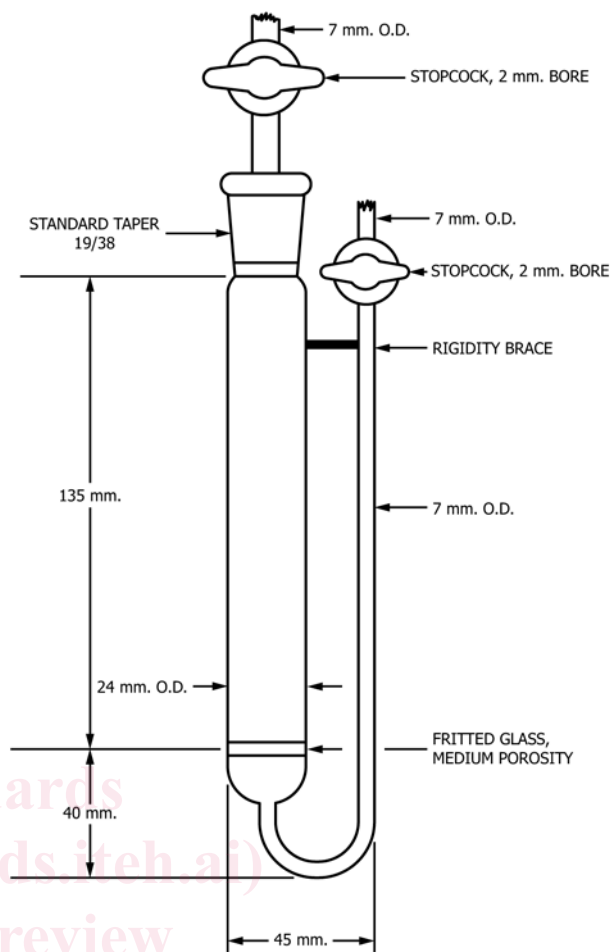


FIG. 1 Radon Bubbler

³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE 1 Radioactive Decay Characteristics of ^{226}Ra and Its Progeny

NOTE 1—Monographie BIPM-5 – Table of Radionuclides, Comments on Evaluations, Vols 1–8, Bureau International des Poids et Mesures, 2016, available from <https://www.bipm.org> or <http://www.lnhb.fr/nuclear-data>.

Radionuclide	Half-Life	Mode of Decay
^{226}Ra	1600 years	α
^{222}Rn	3.8232 days	α
^{218}Po	3.071 min	α
^{214}Pb	26.916 min	β, γ
^{214}Bi	19.8 min	β, γ
^{214}Po	162.3 μs	α
^{210}Pb	22.23 years	β, γ

tube is filled with magnesium perchlorate and the lower half with a sodium hydroxide-coated silica absorbent.

7.5 *Scintillation Counter Assembly*, consisting of a 50 mm (2 in.) or more in diameter photomultiplier tube mounted in a light-tight housing and coupled to the appropriate preamplifier, high-voltage supply, and scaler. A high-voltage safety switch should open automatically when the light cover is removed to avoid damage to the photomultiplier tube. The preamplifier should incorporate a variable gain adjustment. The counter should be equipped with a flexible ground wire which is attached to the chassis photomultiplier tube by means of an alligator clip or similar device. The operating voltage is ascertained by determining a plateau using ^{222}Rn in the scintillation chamber as the alpha source. The slope of the plateau should not exceed 2 %/100 V. The counter and the scintillation chamber should be calibrated and used as a unit when more than one counter is available. The background counting rate for the counter assembly without the scintillation chamber should range from 0.00 to 0.0005 s⁻¹.

7.6 *Membrane Filters*, 0.45 μm pore size.

7.7 *Silicone Grease*, high-vacuum, for bubbler stopcocks.

7.8 *Platinum Ware*, crucibles, 20 to 30 mL, and one 500 mL capacity dish. Platinum ware is cleaned by immersing and

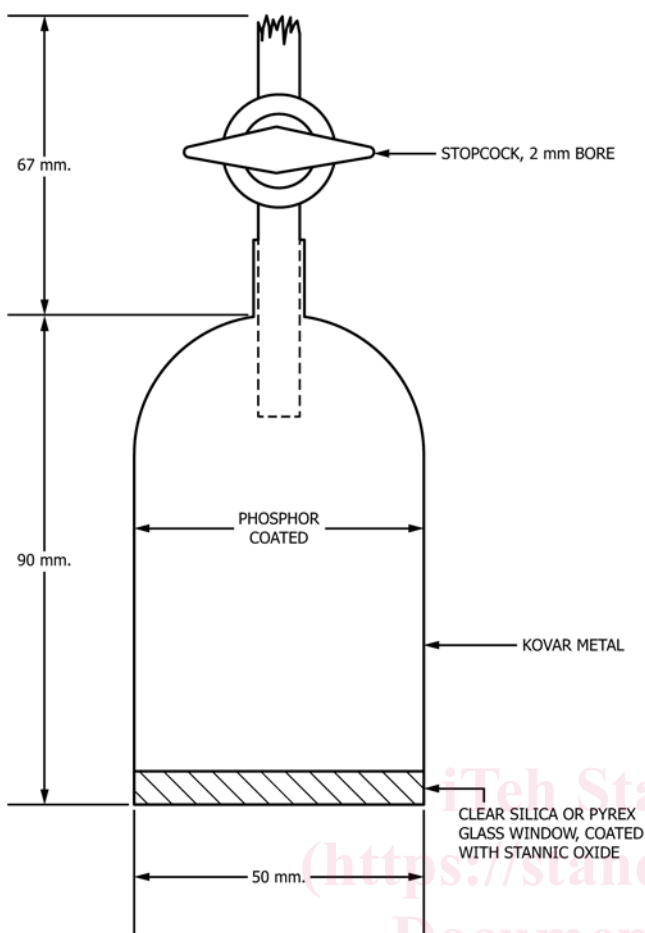


FIG. 2 Radon Scintillation Chamber

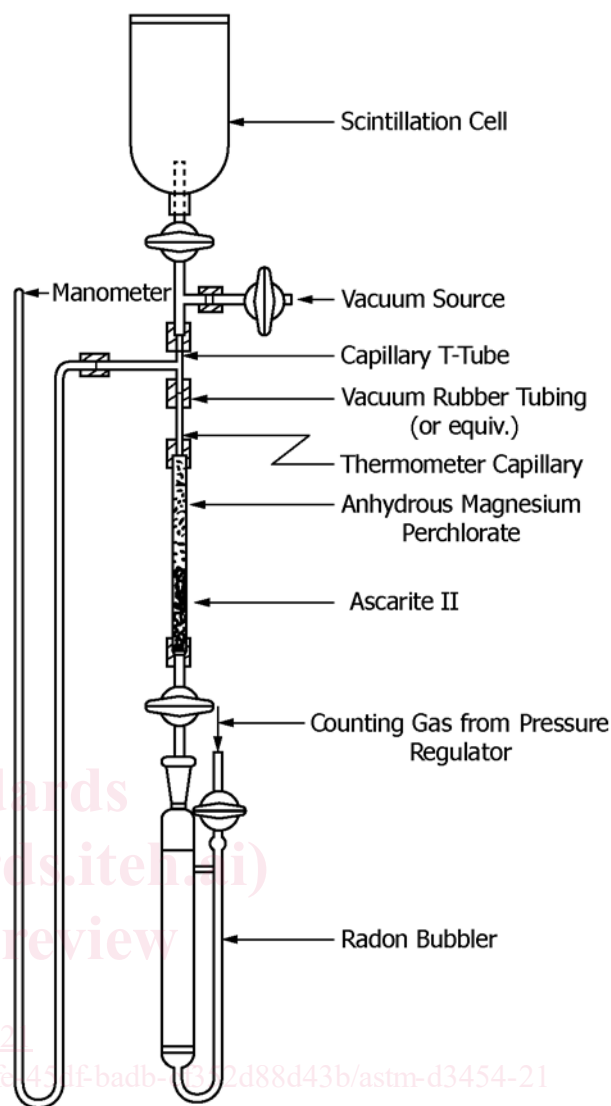


FIG. 3 De-Emanation Assembly

rotating in a molten bath of potassium pyrosulfate, removing, cooling, and rinsing in hot tap water, digesting in hot 6 M hydrochloric acid (HCl), rinsing in water, and finally flaming over a burner.

7.9 *Laboratory Glassware*—Glassware may be decontaminated before and between uses by heating for 1 h in EDTA- Na_2CO_3 decontaminating solution at 90 to 100 °C, then rinsing in water, in 1 M HCl, and again in water.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean conforming to Specification D1193, Type III.

8.3 *Radioactive Purity of Reagents*—Radioactive purity shall be such that the measured results of blank samples do not exceed the calculated probable error of the measurement or are within the desired precision.

8.4 *Ammonium Sulfate Solution (100 g/L)*—Dissolve 10 g of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) in water and dilute to 100 mL.

8.5 *Barium Chloride Carrier Solution Stock (17.8 g/L)*—Dissolve 17.8 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 L. This solution will contain 10 mg/mL Ba^{++} .

8.6 *Barium-133 Tracer Solution*—(approximately 3 kBq/mL).

8.7 *Barium Chloride Carrier Solution, Working*—Add 100 mL of barium chloride carrier stock solution and 10 mL of ^{133}Ba tracer solution to 890 mL of water and mix thoroughly.

This solution will contain approximately 1 g/L of Ba⁺⁺. Allow to stand for 24 h and filter through a membrane filter.

8.8 *EDTA-Sodium Carbonate Decontaminating Solution*—Dissolve 10 g of disodium ethylenediaminetetraacetate and 10 g of sodium carbonate (Na₂CO₃) in water and dilute to 1 L.

8.9 *Flux*—To a large platinum dish (about 500 mL capacity) add 30 mg of BaSO₄, 65.8 g of K₂CO₃, 50.5 g of Na₂CO₃, and 33.7 g of Na₂B₄O₇·10 H₂O. Mix well and heat cautiously until the water is expelled; fuse and mix thoroughly by swirling. Cool flux, grind it in a porcelain mortar to pass a U.S. Standard No. 10 (2.00-mm) (or finer) sieve. Store in an airtight bottle. (Flux can be prepared in smaller batches.)

8.10 *Hydrochloric Acid* (sp gr 1.19)—Concentrated HCl.

8.11 *Hydrochloric Acid Solution 6 M (1 + 1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

8.12 *Hydrochloric Acid Solution 1 M (11 + 1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 11 volumes of water.

8.13 *Hydrochloric Acid Solution 0.24 M (49 + 1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 49 volumes of water.

8.14 *Hydrochloric Acid Solution 0.1 M (119 + 1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 119 volumes of water.

8.15 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated HF. Use extreme caution.

8.16 *Hydrogen Peroxide 3 % (9 + 1)*—Mix 1 volume of hydrogen peroxide (H₂O₂) (30 %) with 9 volumes of water.

8.17 *Magnesium Perchlorate*—Anhydrous magnesium perchlorate (Mg(ClO₄)₂).

8.18 *Phosphoric Acid* (sp gr 1.69)—Concentrated phosphoric acid (H₃PO₄).

8.19 *Radium Standard Solution* (0.37 Bq/mL).

8.20 *Sodium Hydroxide-Coated Silica Absorbent, Proprietary*,⁵ 8 to 20 mesh.

8.21 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H₂SO₄).

8.22 *Sulfuric Acid Solution 0.05 M (359 + 1)*—Mix 1 volume of concentrated H₂SO₄ (sp gr 1.84) with 359 volumes of water. This solution is 0.1 N. Slowly add acid to water.

8.23 *Helium*, in a high-pressure cylinder with a two-stage pressure regulator and needle valve.

9. Sampling

9.1 Collect the sample in accordance with the applicable standards as described in Practices **D3370**.

⁵ The sole source of supply of this material known to the committee at this time is Ascarite II, produced by Arthur H. Thomas Co, Philadelphia, PA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

10. Calibration and Standardization

10.1 Close the inlet stopcock of a bubbler (**Note 1**), add 5 mL of BaCl₂·2H₂O carrier solution, 1 mL of concentrated HCl (sp gr 1.19), 3 mL (1.11 Bq) of standard radium solution and fill the bubbler ²/₃ to ³/₄ full with water.

NOTE 1—Before using, test bubblers by placing about 10 mL of water in them and passing air through them at the rate of 3 to 5 mL/min. This should form many fine bubbles rather than a few large ones. Do not use bubblers requiring excessive pressure to initiate bubbling. Reject unsatisfactory bubblers. Corning's⁶ "medium-porosity" fritted glass disks are usually satisfactory.

10.2 Insert the outlet stopcock into the bubbler with the stopcock open. Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of bubbler and adjust the inlet pressure to produce a froth a few millimetres thick. Establish a zero ingrowth time by purging the liquid with helium for 15 to 20 min.

10.3 In rapid succession, close the inlet stopcock, remove the gas connection, and the close outlet stopcock. Record the date and time and store the bubbler preferably for 2 to 3 weeks before collecting and counting the ²²²Rn.

10.4 Attach a scintillation chamber as shown in **Fig. 3**; substitute a glass tube with a stopcock for the bubbler so that the helium gas can be turned on and off conveniently. Open the stopcock on the scintillation chamber; close the stopcock to the gas and gradually open the stopcock to vacuum source to evacuate the cell. Close the stopcock to the vacuum source and check the manometer reading for 2 min to test the system, especially the scintillation chamber for leaks. If leaks are detected they should be identified and sealed.

10.5 Open the stopcock to the helium gas and allow the gas to enter the chamber slowly until atmospheric pressure is reached. Close all the stopcocks.

10.6 Place the scintillation chamber on the photomultiplier tube (in a light-tight housing), wait 10 min, and obtain a background count rate (preferably over a period of at least 100 min). Phototube must not be exposed to external light with the high voltage applied.

10.7 With the scintillation chamber and bubbler in positions indicated in **Fig. 3** and all stopcocks closed, open the stopcock to vacuum and then to the scintillation chamber. Evacuate the scintillation cell and the gas purification system. Close the stopcock to vacuum and check for leaks as in **10.4**.

10.8 Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of the bubbler.

10.9 Very cautiously open the bubbler outlet stopcock to equalize pressure and transfer all or most of the fluid in the inlet side arm to the bubbler chamber.

10.10 Close the outlet stopcock and very cautiously open the inlet stopcock to flush remaining fluid from the side arm and fritted disk. Close the inlet stopcock.

⁶ A trademark by Corning Incorporated, Corning, NY.

10.11 Repeat steps 10.9 and 10.10 several times to obtain more nearly equal pressure on the two sides of the bubbler.

10.12 With the outlet stopcock fully open, cautiously open the inlet stopcock so that the flow of gas produces a froth a few millimetres thick at the surface of bubbler solution. Maintain the flow rate by adjusting the pressure with the regulator valve and continue de-emanation until the pressure in the scintillation chamber reaches the atmospheric pressure. The total elapsed time for de-emanation should be 15 to 20 min.

10.13 In rapid succession, close the stopcock to the scintillation chamber, close the bubbler inlet and the outlet stopcocks, shut off and disconnect the gas supply. Record the date and time, which is the end of ingrowth and the beginning of decay.

10.14 Store the bubbler for another ^{222}Rn ingrowth in the event a subsequent de-emanation is desired. The standard bubbler containing the standard may be kept and reused indefinitely.

10.15 At least four hours after de-emanation, place the scintillation chamber on the photomultiplier tube, wait 10 min, and count until desired statistical accuracy is achieved. Record the date and time the counting was started and finished.

10.16 Calculate the calibration factor E , for the scintillation chamber as follows:

$$E = \frac{R_N}{A_R \cdot (1 - e^{-\lambda t_1}) \cdot e^{-\lambda t_2}} \quad (1)$$

where:

R_N = net count rate, s^{-1} (standard – background),

A_R = activity of ^{226}Ra in the bubbler (Bq),

t_1 = ingrowth time of ^{222}Rn (h),

t_2 = decay time of ^{222}Rn occurring between de-emanation and the midpoint of counting (h), and

λ = decay constant of ^{222}Rn (0.00755 h^{-1}).

NOTE 2—A slightly more accurate correction for decay during a long counting period is included in the following equation:

$$E = \frac{R_N}{A_R \cdot (1 - e^{-\lambda t_1}) \cdot e^{-\lambda t_2}} \cdot \frac{\lambda t_3 / 2}{\sinh(\lambda t_3 / 2)} \quad (2)$$

where:

t_3 = elapsed time (real time) between beginning and end of the count (h).

10.17 Carry out the background measurements prior to each sample measurement. Perform calibrations with each scintillation chamber used, and repeat at least annually or when calibration verification shows an unacceptable change in efficiency.

10.18 To remove ^{222}Rn and prepare the scintillation chamber for reuse, evacuate and cautiously refill with helium. Repeat this evacuation and refilling twice. For chambers containing high activities of ^{222}Rn , repeat the procedure more often.

11. Procedure

11.1 Soluble ^{226}Ra :

11.1.1 Filter the sample through a membrane filter. Take a 1 L aliquot, or a smaller volume so as not to exceed 1.11 Bq of ^{226}Ra , and transfer to a 1500 mL beaker. Acidify with 20 mL

of concentrated HCl (sp gr 1.19) per litre of filtrate, heat, and add with vigorous stirring 50 mL of BaCl_2 working carrier solution. For sample volumes less than a litre, dilute to 1 L with 0.24 M HCl prior to the addition of carrier.

11.1.2 Cautiously and with vigorous stirring, add 20 mL of H_2SO_4 (sp gr 1.84). Cover the beaker and allow to stand overnight.

11.1.3 Filter the supernate through a membrane filter, using 0.05 M H_2SO_4 to transfer the Ba-Ra precipitate to the filter. Wash the precipitate twice with 0.05 M H_2SO_4 .

11.1.4 Place the filter in a platinum crucible, add 0.5 mL of concentrated HF (sp gr 1.15) and 3 drops (0.15 mL) of $(\text{NH}_4)_2\text{SO}_4$ solution, and evaporate to dryness.

11.1.5 Carefully ignite the filter and residue over a small flame until the carbon is burned off (after charring of filter, a Meker burner may be used).

11.1.6 Cool, add 1 mL of concentrated H_3PO_4 (sp gr 1.69), and heat on a hot plate to about 200 °C. Gradually raise temperature to about 300 to 400 °C for 30 min.

11.1.7 Swirl the crucible over a low Bunsen flame, adjusted to avoid spattering. Swirl so that the crucible walls are covered with hot concentrated H_3PO_4 (sp gr 1.69). Continue to heat until the BaSO_4 dissolves to give a clear melt (just below redness), and then heat for 1 min more to ensure removal of SO_3 .

11.1.8 Cool, fill the crucible one-half full with 6 M HCl, heat on a steam bath, then gradually add the water to within 2 mm of the top of the crucible.

11.1.9 Evaporate on the steam bath until there are no more vapors of HCl.

11.1.10 Add 6 mL of 1 M HCl, swirl, and warm to dissolve the BaCl_2 crystals.

11.1.11 Close the inlet stopcock of a greased and tested radon bubbler. Add a drop of water to the fritted disk and transfer the sample from the platinum crucible to the bubbler using a medicine dropper. Rinse the crucible with at least three 2 mL portions of water. Add water until the bubbler is $\frac{2}{3}$ to $\frac{3}{4}$ full.

11.1.12 De-emanate the solution in accordance with 10.2 and 10.3.

11.1.13 After 3 weeks of ^{222}Rn ingrowth, de-emanate and count as described in 10.7 through 10.15.

11.1.14 Transfer the solution in the bubbler to a gamma-counting container. Wash the bubbler thoroughly with 1 M HCl and combine with the sample in a container. Measure the ^{133}Ba activity in a gamma-ray counter. For a discussion of gamma ray counting refer to Practice D3649. Calculate the sample yield, Y , by dividing the ^{133}Ba activity of the sample by the ^{133}Ba activity of a 50 mL aliquot of BaCl_2 carrier working solution counted under identical conditions of volume and geometry as the sample.

11.1.15 The sample may be stored for a second ingrowth or discarded and the bubbler cleaned for reuse. A thorough rinsing with 0.24 M HCl is a satisfactory cleaning procedure. If however, the ^{226}Ra in a bubbler exceeded 0.37 Bq (10 pCi), a more rigorous cleaning may be necessary. Remove the stopcock grease, using a cloth and solvent, and then immerse for 1 h in hot (90 to 100 °C) EDTA – Na_2CO_3 solution. Heat the