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RADIOCHEMICAL ANALYTICAL PROCEDURES FOR ANALYSIS OF ENVIRONMENTAL SAMPLES

U.S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

March 1979

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for the
U.S. DEPARTMENT OF ENERGY

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RADIOCHEMICAL ANALYTICAL PROCEDURES FOR ANALYSIS OF ENVIRONMENTAL SAMPLES

Edited by

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ABSTRACT

This manual is a compilation of the chemical and physical procedures used at the Environmental Monitoring and Support Laboratory-Las Vegas for determining radionuclides in environmental surveillance samples. It supersedes the "Handbook of Radiochemical Analytical Methods" published as EPA-680/4-75-001 in February 1975.

It should be noted that the procedures in the current compilation are intended for use in processing relatively large numbers of samples in the shortest possible time for environmental radiological surveillance and, therefore, in some cases represent a compromise between precise analytical determination and adequate determination for surveillance purposes.

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DETERMINATION OF GROSS ALPHA AND BETA IN WATER

1. Principle

1.1 All natural waters contain varying amounts of radioactivity, either natural or man-made. A screening technique is used to determine the quantities of alpha or beta emitting radionuclides present. A known volume of sample is concentrated, dried in a planchet and counted in a low-background internal proportional counter. The activity determined by this method is not indicative of any specific nuclide. Tritium and other volatile radionuclides (for example, radioiodine) cannot be determined by this method.

2. Application

2.1 The method is applicable for the analysis of either total, dissolved, or suspended solids in water for gross alpha and beta.

3. Range

3.1 No range has been established.

4. Interferences

4.1 The evaporated sample residue, by acting as an absorber for the alpha and beta particle, is the largest interference. Moisture absorbed or trapped by the residue also serves as an interference.

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.

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

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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

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

6. Precision and accuracy

6.1 Gross alpha and beta measurements by this method have an inherent inaccuracy in that samples may contain alpha and beta emitters with energies different from the calibration standards. In such circumstances, the counting efficiencies (cpm/dpm) used will not produce accurate information for the radionuclides in the sample. Therefore, this method is, at best, good only for semiquantitative analysis. The importance of precision (or repeatability) is that a given water source may be checked periodically for gross alpha and beta and any significant changes in the results from one time to the next may require specific analysis. It is necessary then that such changes be real and not a result of poor precision.

6.2 Analytical results of spiked water containing 50 pCi cesium-137 and 5 pCi/liter americium-241 indicate accuracies with deviations from known values of less than 10% at the 95% confidence level.

7. Shipment and storage of samples and sample stability

7.1 Samples for gross alpha and beta analysis must be preserved with 20 ml of concentrated nitric acid per 3.7 liters. However, judgment must be made before acidifying as to type of analysis desired. If total gross alpha and beta are required, the acid treatment must be made at time of sampling. If a differentiation between dissolved versus suspended radionuclides is desired, the sample should be filtered in the field, acid added to the aqueous portion and the two fractions submitted to the laboratory.

7.2 With proper preservation the storage time of the sample depends entirely on the half-life of the contained radionuclides.

8. Reagents

8.1 Alcohol, ethyl: 95% reagent grade

8.2 Nitric acid, concentrated: 70% reagent grade

8.3 Nitric acid, 3N: Add 187 ml concentrated nitric acid to 600 ml distilled water. Cool, and dilute to 1000 ml.

9. Apparatus

9.1 Beakers: 250 ml

9.2 Cylinder, graduated: 200 ml

9.3 Hot plate

9.4 Low-background, thin-window proportional counter

9.5 Planchets: 2-inch

10. Procedure

10.1 Transfer a 200-ml portion of the well-shaken acidified sample to a 250-ml beaker. If the sample has not been filtered and the activity of the suspended solids is required, filter a 1000-ml portion through a Whatman No. 2 filter paper. Add a 200-ml portion of the filtrate to a 250-ml beaker.

10.2 Add 10 ml concentrated nitric acid and evaporate slowly to near dryness. Quantitatively transfer to a tared planchet using 3N nitric acid. Evaporate and dry at 105° C. Cool. Weigh for self-absorption correction and count for 50 minutes in the low-background proportional counter.

10.3 Place the filter (either from the field or laboratory) in a tared planchet, saturate with ethyl alcohol and ignite. Cool, weigh for self-absorption correction and count for 50 minutes in a low-background proportional counter.

11. Calibration

Counting efficiency of the low-background beta counter is determined by three factors: geometry, backscatter, and self-absorption. The first two, geometry and backscatter, are fairly well established for each instrument, while the third, self-absorption, is dependent on the sample. Therefore, "self-absorption curves", similar to the curves illustrated in Figure 1, must be prepared. Samples with known activity but with varying sample weights are prepared and the data plotted as indicated in Figure 1. The cesium-137 and americium-241 standards are both traceable to the National Bureau of Standards.

11.1 Prepare reference data for counting efficiency versus water solids by adding known amounts of standard cesium-137 to varying aliquots of tap water. Add 5 ml concentrated nitric acid.

11.2 Evaporate to near dryness and quantitatively transfer to a tared planchet. Dry and heat to 105° C. Cool and reweigh.

11.3 Repeat 11.1 and 11.2 using americium-241.

11.4 Count gross beta standard for 50 minutes and gross alpha standards for 100 minutes.

11.5 Correct counting data for background and plot counting efficiency versus mg of solids on planchet.

11.6 Calculate % alpha activity that is detected in beta channel of counter.

12. Quality control

12.1 Every tenth sample is reprocessed as a blind duplicate, and bi-monthly cross-check samples are obtained from the Quality Assurance Branch, EMSL-LV. A close evaluation of these data is made and corrective action taken as indicated.

13. Calculations

13.1 Gross alpha (pCi/l) = $\frac{A}{2.22\ EV}$

where A = net counts per minute
2.22 = dpm/pCi
E = fractional counting efficiency (obtained from calibration curve)
V = volume (liters)

13.2 Gross beta (pCi/liter) = $\frac{A - (DA)}{2.22\ EV}$

where A = net counts per minute
D = fraction of alpha activity
2.22 = dpm/pCi
E = fractional counting efficiency (obtained from calibration curve)
V = volume of sample (liters)

14. References

14.1 Handbook of Radiochemical Analytical Methods, EPA-680/4-75-001 February 1975.

14.2 Tentative Reference Method for the Measurement of Gross Alpha and Gross Beta Radioactivities in Environmental Waters, EPA-680-4/75-005, June 1975.

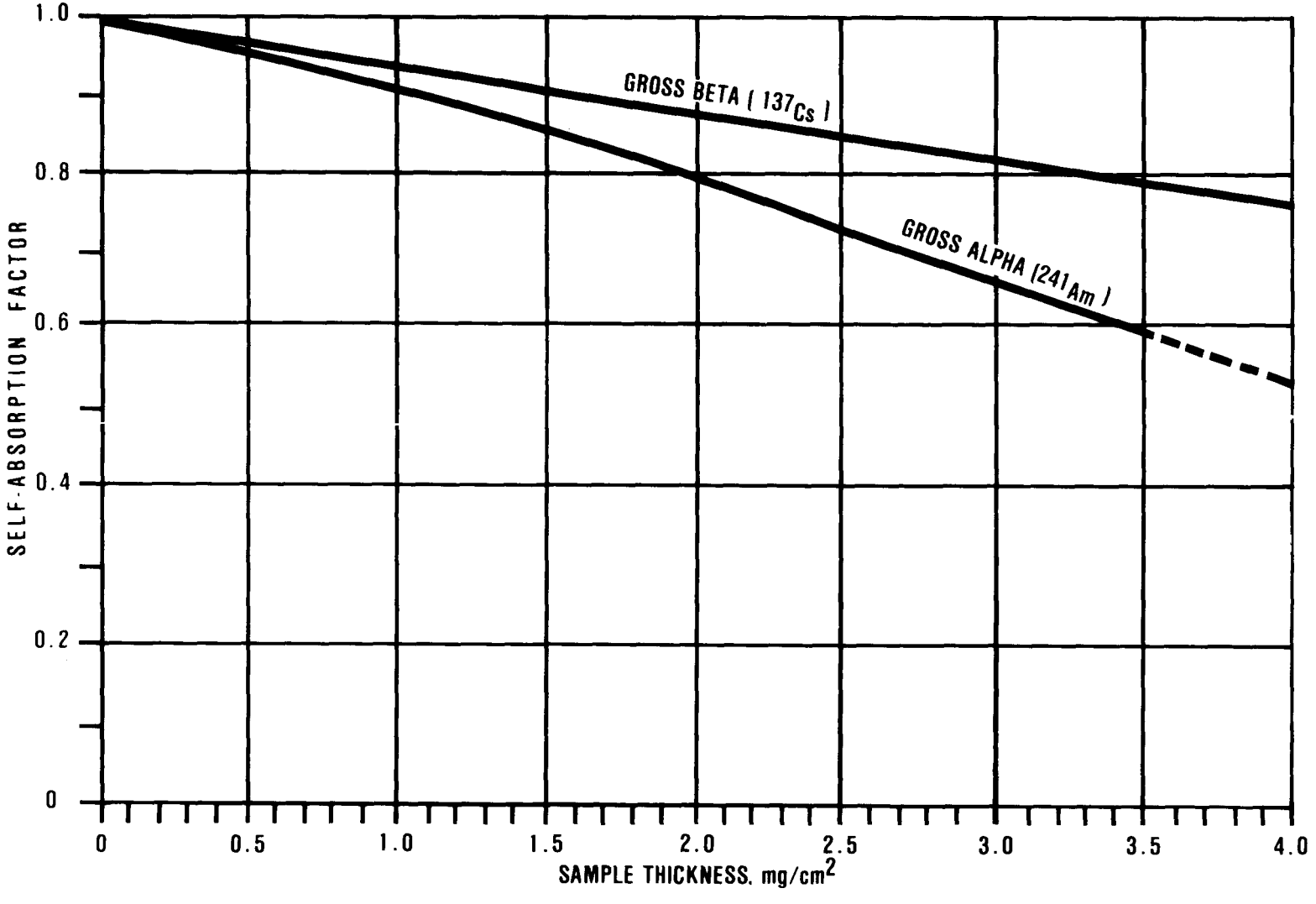

Figure 1. Typical Adsorption Curves.

DETERMINATION OF GROSS BETA ACTIVITY IN AIRBORNE PARTICULATES

1. Principal

1.1 All airborne particulate samples contain both natural and man-made radioactivity. A screening technique is used to determine the quantities of beta-emitting nuclides. Based on results obtained from this screening technique, the need for radiochemical analysis is determined.

2. Application

2.1 This method is applicable for determination of gross beta concentration of airborne particulates collected on a filter, or any other material collected on a filter, where self-absorption can be ignored (for example, swipes).

3. Range

3.1 In reality there is no upper range. A practical upper range is approximately 5×10^5 beta counts per minute. Above this level, there is a significant decrease in counting efficiency.

4. Interferences

4.1 Since this is a gross analysis, there are no interferences from other nuclides. Samples collected over a long period of time, or samples collected in an area with a high concentration of airborne particulate matter, may result in filter overloading. Part of the collected particulate matter may then flake off the filter, yielding a nonrepresentative sample.

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.

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

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 (α) = .05

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

S_b = standard deviation of the background
2.22 = dpm/pCi
E = fractional counting efficiency
S = sample size

6. Precision and accuracy

6.1 Inaccuracies are primarily attributable to samples containing beta emitters of different energies than the calibration standards, a large amount of particulate matter being accumulated on the filter creating some self-absorption, and some of the collected particulate matter flaking off the filter.

6.2 Analyzing filters containing known amounts of strontium-90 and cesium-137 produces results within 10% of the known value at the 95% confidence level. For standard samples close to background, the 95% confidence interval is approximately 5 pCi per filter.

7. Shipment and storage of samples and sample stability

7.1 Most filters are received in the mail. Therefore, careful handling is not of prime consideration.

8. Reagents

8.1 No reagents are used.

9. Apparatus

9.1 Proportional beta counter with 12.7-cm window

9.2 Filters; various types as required. No larger than 10.2 cm.

10. Procedure

10.1 Air filter samples with their field data sheets enclosed are received in the mail and their receipt date is documented.

10.2 The air filter is placed in a glassine envelope. The information from the field data sheet is then recorded on an IBM Hollerith punch card. The filter, data sheet, and punch card, along with two duplicate punch cards, are sent to the gross beta counting room.

10.3 Three beta counts are made. The first count is made when the sample is received in the counting room, the second count is made at the date of collection plus 5 days, and the third count is made at the date of collection plus 12 days. If the sample has not been received by the date of collection plus 4 days, the first count is cancelled. If the sample is received after the date of collection plus 5 days, the sample receives an initial beta count upon receipt and a second beta count 7 days later.

10.4 If the initial beta count exceeds 50 counts per minute, an isotopic analysis by gamma spectroscopy is performed.

10.5 A daily gross beta report is compiled based on the gross beta analyses completed on the previous day.

10.6 The last 2 beta counts are used to calculate a gross beta concentration at the midpoint of collection. This extrapolated gross beta concentration is compiled each month into a monthly gross beta report, containing the results for all air sampling stations active during that month.

11. Calibration

11.1 A 10-cm diameter glass-fiber filter is sprayed with 6 coats of Krylon and then mounted on an 11 1/2-cm diameter stainless steel planchet. A calibrated NBS strontium-90, yttrium-90 standard is pipetted uniformly over the surface of the filter resulting in a standard filter containing approximately 2.0×10^4 disintegrations per minute of strontium-90 and yttrium-90.

11.2 The standard filter is beta-counted.

11.3 Counting efficiency $= \dfrac{\text{net counts per minute}}{\text{dpm of standard}}$

12. Quality control

12.1 Each morning a background and a strontium-90, yttrium-90 standard are counted. The results are recorded and appropriate quality control charts are maintained.

13. Calculations

13.1 Daily gross beta concentration

$$\text{Gross beta } (\text{pCi/m}^3) = \frac{\text{cpm}}{2.22\ E\ V}$$

where cpm = gross counts-bkg counts/counting time
2.22 = dpm/pCi
E = counting efficiency
V = sample volume (m^3)

13.2 Monthly gross beta concentration

$$\text{Gross beta } (\text{pCi/m}^3) = A_2 \left(\frac{T_A}{T_A - (T_2 - T_c)} \right)^{1.2}$$

where

A_2 = gross beta activity (pCi/m^3) from the sample collection plus 5-day beta count

$$T_A = \frac{T_3 - T_2}{\left(\frac{A_2}{A_3}\right)^{0.835} - 1}$$

A_3 = gross beta activity (pCi/m^3) from the sample collection plus 12-day beta count

T_c = date of midpoint of sample collection

T_2 = date of sample collection plus 5-day beta count

T_3 = date of sample collection plus 12-day beta count

T_A is the estimated age of the fission product material collected on the filter at T_2. If the date of fission is known, rather than estimating T_A, the date may be entered into the computer program MBETA75 via a control card for the exact calculation of T_A. Also, the value of the exponent of 1.2 in the gross beta calculation formula can be changed by changing a single FORTRAN statement.

DETERMINATION OF RADON-222 IN AIR, WATER, AND NATURAL GAS

1. Principle

1.1 Radon-222, the first decay product of radium-226, occurs in various amounts in all geological formations. It is constantly being released to the atmosphere. The half-life of radon-222 is 3.825 days. Therefore, a fairly fast method of analysis is required for its determination. Direct alpha scintillation counting is possible if the radon-222 levels are above 2 pCi/liter. If radon-222 levels are less than 2 pCi/liter, a concentration step must be incorporated.

1.2 The decay of radon-222 leads to two additional short-lived alpha-emitting progeny. These two isotopes will ingrow to 97% of equilibrium in 4 1/2 hours, and will thus lead to an increase in count rate. Theoretically, 1 pCi of radon-222 at equilibrium should have a disintegration rate of 6.6 counts per minute.

2. Application

2.1 This method is applicable for the determination of radon-222 in air, water, and natural gas.

3. Range

3.1 No upper range has been established; however, samples of air and water have been analyzed that have contained 6×10^5 pCi/liter radon-222.

4. Interferences

4.1 Other alpha-emitting gaseous nuclides will interfere. The principle interference is radon-220, which can be eliminated by allowing it to decay and filtering out the daughter products.

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.

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

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* 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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision

6.1 The precision at 1 pCi/liter is estimated at $\pm$ 20% below 1 pCi/liter and $\pm$ 10% above 1 pCi/liter.

7. Shipment and storage of samples and sample stability

7.1 Shipment to the laboratory must be by the most expeditious method. The analysis must be performed as soon as possible for all sample types.

7.2 It is impossible to store any of the sample types because of the short half-life of the radon-222.

8. Reagents

8.1 Ascarite, 20 to 30 mesh.

8.2 Charcoal, coconut, 4 to 10 mesh.

8.3 Drierite, 10 to 20 mesh.

8.4 Helium, purified, store for 6 months or longer.

9. Apparatus

9.1 A manifold system as illustrated in Figure 2.

9.2 T_1 is a steel ball trap.

9.3 D_1 is an Ascarite and Drierite trap.

9.4 C_1 and C_2 are charcoal traps.

9.5 Scintillation cell.

9.6 Alpha scintillation counter.

9.7 Vacuum pump.

LIQUIDS

9.8 An apparatus for radon de-emanation as illustrated in Figure 4.

10. Procedure

GASES

Samples are usually collected in a 30-liter Tedlar bag, a 2-liter glass flask, or as a compressed gas.

10.1 Attach sample container to the "sample-in" line (Figure 1). Evacuate all lines, bulb A, and scintillation cell 1. Record room pressure and temperature.

10.2 Transfer all of the 2-liter sample to bulb A, or bring bulb A to atmospheric pressure with the bag sample or compressed gas sample.

10.3 Fill scintillation cell 1, located at B (Figure 2), with sample.

10.4 Immediately count scintillation cell for 30 minutes. If count rate is 0.3 cpm or greater, prepare a duplicate as in 10.3. Hold cell for 4 1/2 hours to allow radon and its progency to reach equilibrium and count for 30 minutes.

10.5 If count rate is less than 0.3 cpm, continue by adding an ice water bath to T_1, and a dry ice acetone (DIA) bath to C_1 and C_2.

10.6 Establish flow, bulb A → T_1 → D_1 → C_1 → C_2 → vacuum; continue flow until pressure in bulb A returns to room pressure.

10.7 Close all stopcocks and turn off vacuum pump.

10.8 Remove DIA from C_1 and replace with a furnace preheated to 350° C. Establish flow helium → C_1, allow helium to mix in C_1 for one minute. Transfer helium and radon to scintillation cell.

10.9 Repeat 10.8 five times, then establish flow helium → C_2 and repeat 10.8 five times. Do not exceed atmospheric pressure in the scintillation cell.

10.10 Place cell in radon counting apparatus and count at 30-minute intervals until the ingrowth of the radon daughters is complete.

NATURAL GAS

10.11 Attach sample bottle to "sample-in" through an Ascarite-Drierite drier tube.

10.12 Evacuate all transfer lines and scintillation cell. Check for leaks. Gradually open regulator valve and transfer sample to scintillation cell. Record pressure and temperature. Three cells should be prepared for triplicate analysis.

10.13 Place cells in radon counting apparatus and count at 30-minute intervals until the ingrowth of the radon daughters is complete.

WATER

Sampling for radon in water is the most important facet. The solubility of radon in water depends on the temperature, pressure, the concentration of other gases, and dissolved solids. Therefore, in sampling, all of these parameters must be maintained. The use of a radon bubbler (Figure 3) to collect the samples is necessary.

A. From a flowing pipe:

Attach a length of tubing to the sampling valve and place it in the bubbler. Carefully open valve and allow the water to overflow the bubbler. Allow flow for 5 minutes. Seal bubbler immediately and return to laboratory for analysis. Do not allow air space in bubbler.

B. From an open body of water:

Evacuate the bubbler and immerse completely. Open and close the valves while under water. Return the bubbler to the laboratory for analysis.

10.14 Figure 4 illustrates the apparatus for radon transfer from the bubblers. Weigh and attach the bubbler containing the sample to the expansion bulb.

10.15 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, and repeat system integrity check.

10.16 Open stopcocks 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 10.15.

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

10.18 Start de-emanation 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.

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

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

10.21 Remove and clean the bubbler. Reweigh for sample size.

11. Calibration

RADON IN AIR AND NATURAL GAS

Known amounts of radon are added to various volumes of air or natural gas and analyzed by the applicable method.

11.1 Dilute a National Bureau of Standards radium-226 standard to 100 pCi/liter with distilled water.

11.2 Transfer 10 ml of this diluted standard to a radon bubbler and seal.

11.3 After allowing the radon-222 to ingrow to equilibrium with the parent radium-226 (approximately 30 days) de-emanate into a two-liter flask using either compressed air or natural gas.

11.4 Use the appropriate method to analyze for radon-222.

11.5 $$\text{Cell Factor} = \frac{\text{cpm at equilibrium}}{\text{pCi of standard}}$$

WATER

11.6 Using the diluted standard in 11.2, allow the radon-222 to equilibrate, de-emanate into a scintillation cell. Hold for 4 1/2 hours before counting.

11.7 $$\text{Cell Factor} = \frac{\text{cpm at equilibrium}}{\text{pCi of standard}}$$

12. Quality Control

12.1 Every tenth air sample is analyzed in duplicate, and natural gas samples are routinely analyzed in triplicate.

12.2 The sample for radon-222 in water is destroyed during analysis. Therefore, the collection of duplicates is necessary.

13. Calculations

13.1 Air and natural gas

$$\text{Radon-222 (pCi/liter)} = \frac{A}{F \times S}$$

where A = net counts per minute
F = cell factor
S = sample size, liters

13.2 Water

$$\text{Radon-222 (pCi/liter)} = \frac{A}{F \times S}$$

where A = net counts per minute
F = cell factor
S = sample size, kilogram

13.3 For reporting purposes, the radon-222 calculated in 13.1 and 13.2 is back calculated to mid-point of collection.

$$\text{Radon-222 (pCi/liter)}_{\text{Mid-point of collection}} = \text{radon-222} \times e^{\lambda t}$$

where λ = .00755 hours or .18127 days
t = time since mid-point of collection

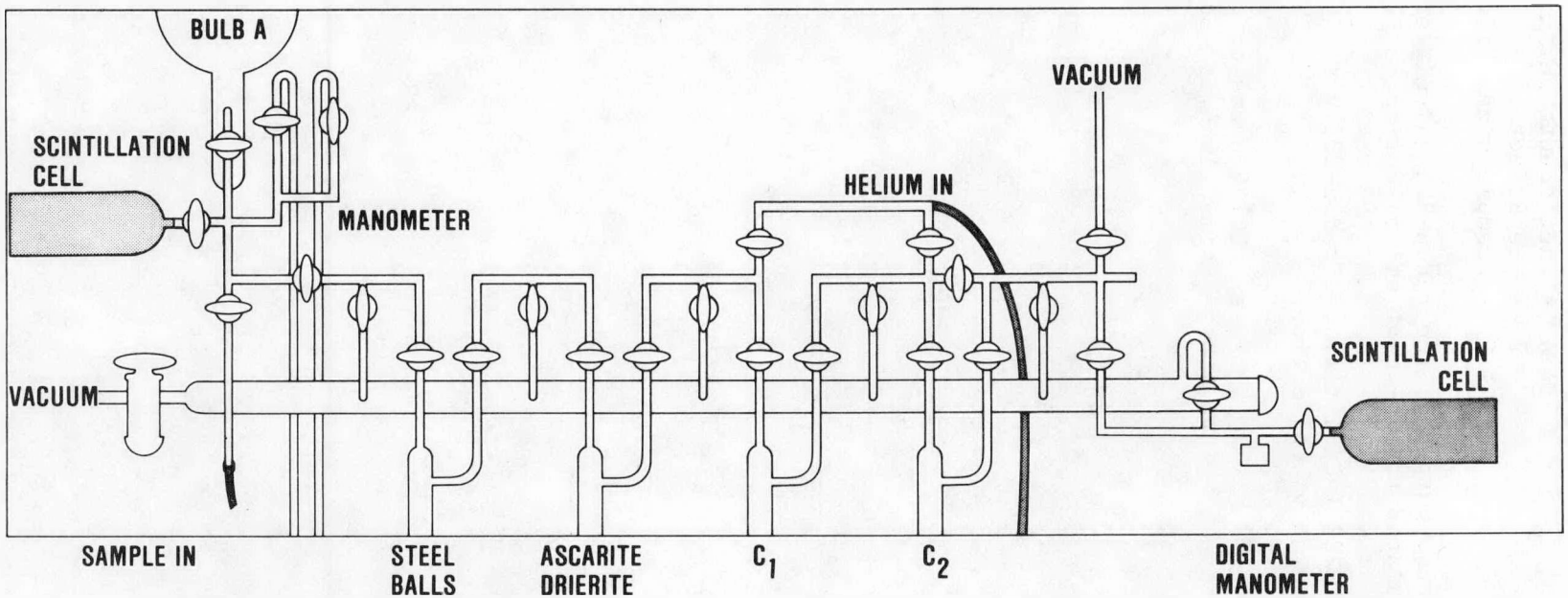

Figure 2. Radon Separation Apparatus.

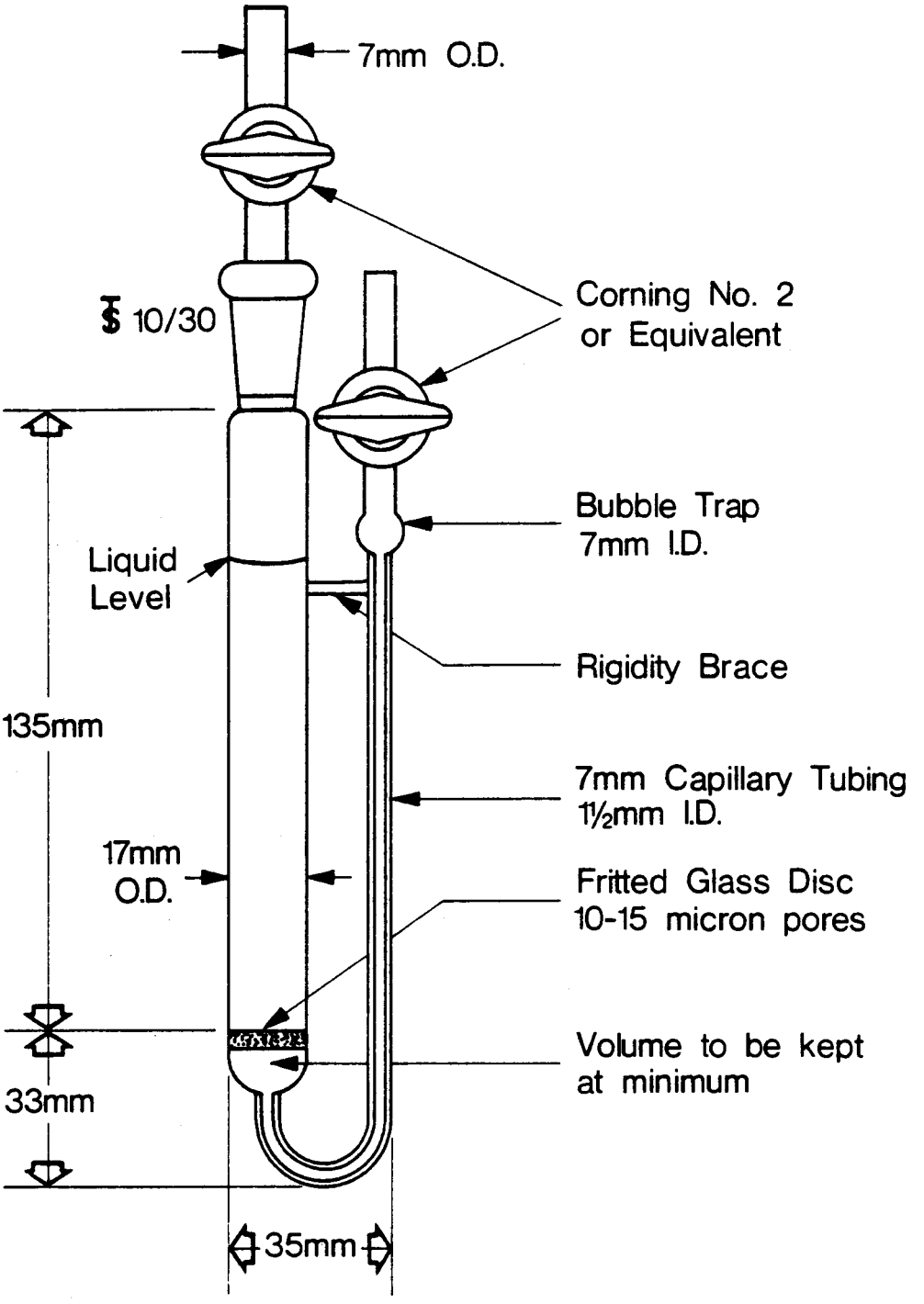

Figure 3. Radon Bubbler.

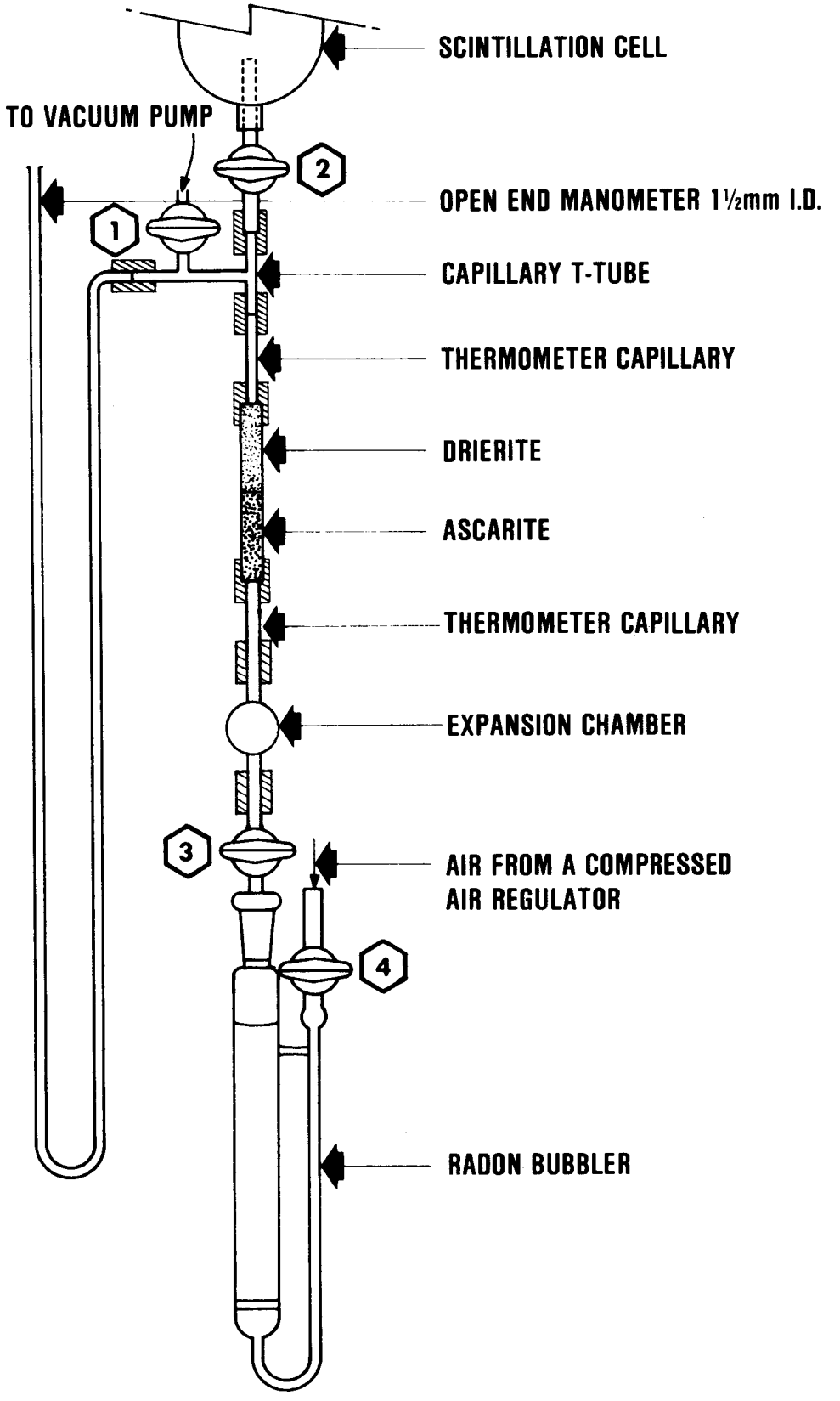

Figure 4. Radon Emanation Apparatus.

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 radium-228 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 ($T_{1/2}$ = 1602 years) decays by alpha emission to radon-222. Radon-222 ($T_{1/2}$ = 3.825 days), a noble gas, is separated and collected from the liquid by a de-emanation technique. The radon-222 is counted by alpha scintillation 4 1/2 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 ($T_{1/2}$ = 6.1 years) is a beta emitter and decays to actinium-228 ($T_{1/2}$ = 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 ($T_{1/2}$ = 11.43 days) and radon-219 ($T_{1/2}$ = 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.

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

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

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 (α) = .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_5DTPA), 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_5DTPA) 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_5DTPA 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 then slowly 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.

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 Na_5DTPA 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 ml 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 1 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 g 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

$$\text{Radium-228 (pCi/liter or g)} = \frac{A}{2.22 \times EY \times (1-e^{-\lambda t_1}) \times (e^{-\lambda t_2}) \times V}$$

where A = net counts per minute
2.22 = disintegration per minute/pCi
EY = combined fractional counting efficiency and chemical yield
t_1 = $T_2 - T_1$ (ingrowth of actinium-228) (hours)
t_2 = $T_3 - T_2$ (decay of actinium-228) (hours)
λ = $\ln 2/T_{\frac{1}{2}}$ = 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.

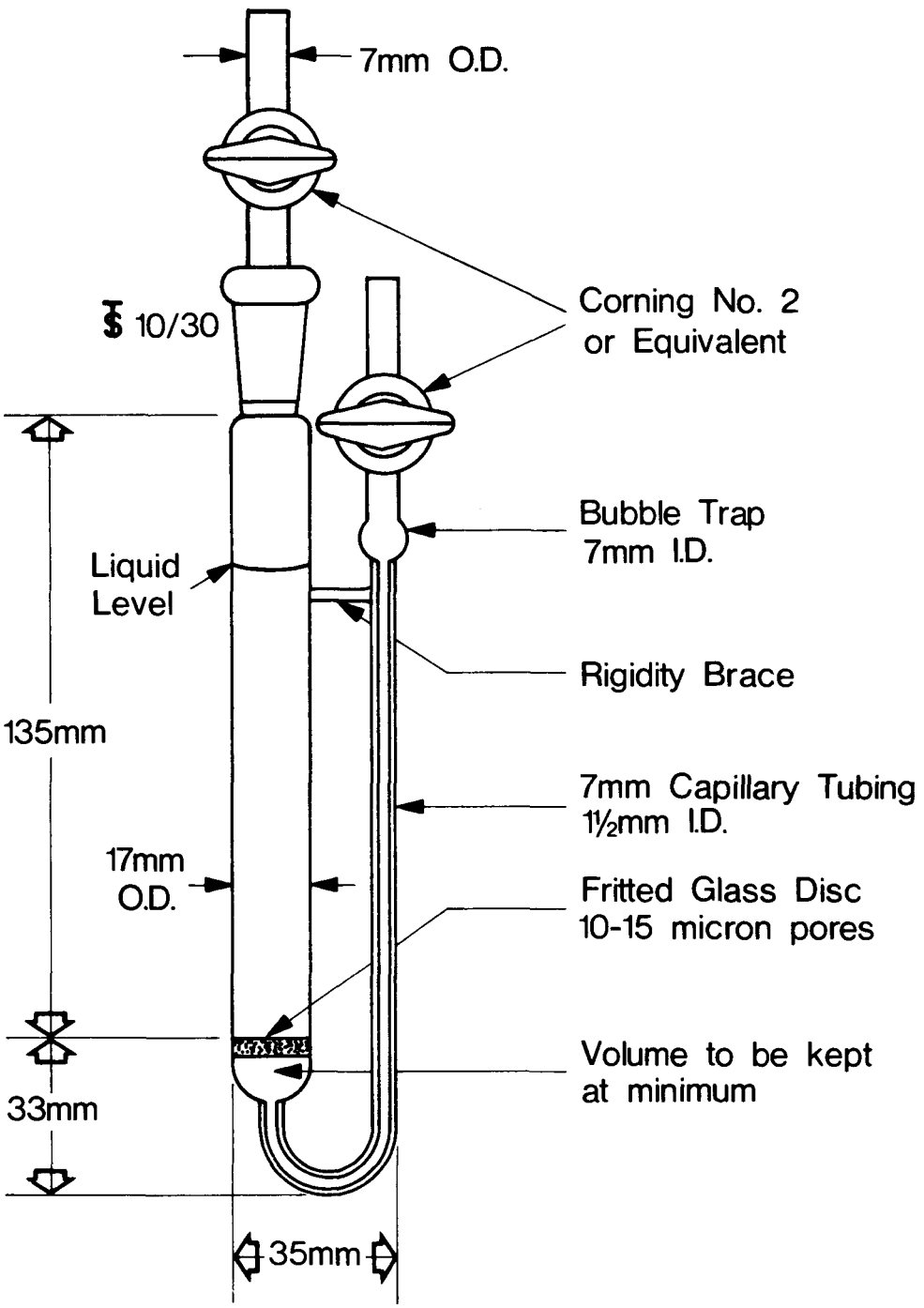

Figure 5. Radon Bubbler.

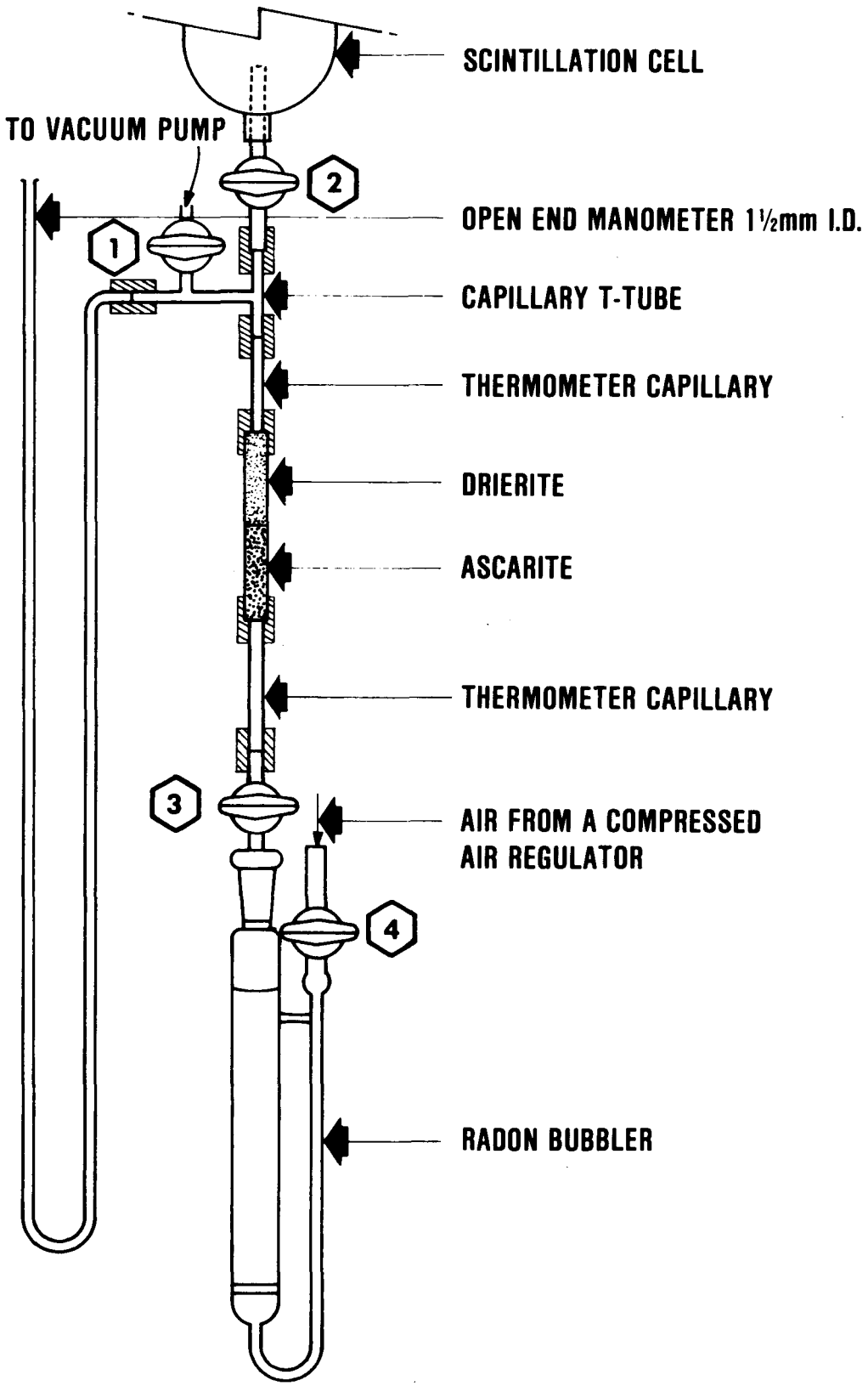

Figure 6. Radon Emanation Apparatus.

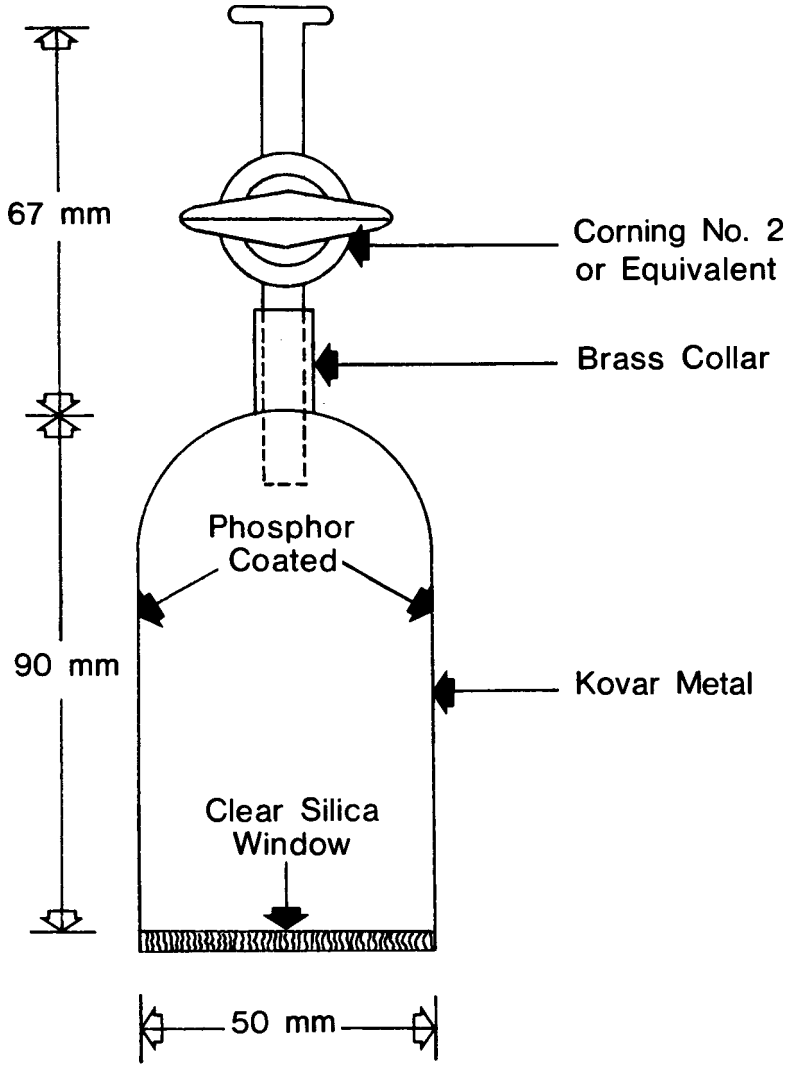

Figure 7. Lucas Scintillation Cell.

ISOTOPIC DETERMINATION OF PLUTONIUM, URANIUM, AND THORIUM IN WATER, SOIL, AIR, AND BIOLOGICAL TISSUE

1. Principle

1.1 Samples are decomposed utilizing techniques of nitric-hydrofluoric acid digestion or ignition. The residues are dissolved in dilute nitric acid and successive sodium and ammonium hydroxide precipitations are performed in the presence of boric acid to remove fluoride and soluble salts. The hydroxide precipitate is dissolved, the solution is adjusted to 9N in hydrochloric acid, and plutonium and uranium are adsorbed on an anion exchange column; separating them from thorium. Plutonium is eluted with hydrobromic acid. Iron is removed from the column by washing with hydriodic acid and the uranium is eluted with dilute hydrochloric acid. The thorium is converted to a nitrate form and adsorbed on the same anion exchange column, separating it from calcium and other interferences. The thorium is then eluted with 9N hydrochloric acid. The actinides are electrodeposited on stainless steel discs from an ammonium sulfate solution and subsequently counted by alpha spectrometry. Chemical yields are determined by the recovery of internal tracer standards (plutonium-236, uranium-232, and thorium-234) added at the beginning of the analysis.

2. Application

2.1 This method is appropriate for the analysis of isotopic plutonium, uranium, and thorium, together or individually, in soil, water, air filters, urine, or ashed residues of vegetation, animal tissues, and bone.

3. Range

3.1 This method is designed to detect environmental levels of activity as low as 0.02 picocuries per sample. To avoid possible cross-contamination, sample activities should be limited to 25 picocuries or less.

3.2 Optimum sample sizes for each of the sample types are listed below. Smaller samples may be analyzed with a commensurate loss in sensitivity. Larger samples may introduce interferences and insoluble residues which prevent satisfactory analysis.

3.3

Sample Type	Optimum Size
Animal tissue ash	10 grams
Bone ash	10 grams
Vegetation ash	10 grams
Soil	10 grams

Sample Type	Optimum Size
Glass-fiber filters	12-4" circles or 1-8" x 10" rectangle
Organic filters	12-4" circles
Water	1 liter
Urine	1 liter

4. Interferences

4.1 Internal tracer standards must be purified at intervals to remove progeny which might contribute to background activities or interfere with subsequent analyses. Thorium-228 will be present in aged plutonium-236 or uranium-232, which must be compensated for, if thorium-228 is to be determined.

4.2 If present, lead-210 will be co-plated with plutonium giving rise to alpha interference by ingrowing polonium-210. This can be minimized by counting the sample within a few days of separation before sufficient polonium-210 ingrowth has occurred.

4.3 Samples containing high levels of phosphate, such as fertilizer, or high levels of barium sulfate, as in glass-fiber filters, may result in low actinide yields.

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.

$$LLD = \frac{3.29\ S_o}{2.22 \times E \times S}$$

where $3.29 = K_\alpha + K_\beta$

K_α = the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present (α) = 0.05

K_β = corresponding value for the predetermined degree of confidence for detecting the presence of activity ($1-\beta$) = 0.95

S_o = estimated standard error for the net sample activity

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

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

7. Shipment and storage of samples and sample stability

7.1 Vegetation, urine, and animal tissue samples should be preserved by refrigeration, freezing, or the addition of formaldehyde until ashing takes place. Water should be acidified with 20 ml concentrated nitric acid per 3.7 liters of sample. Soil, air filters, and ash may be stored indefinitely.

8. Reagents

8.1 Alkaline ethyl alcohol: Adjust the pH of 95% ethanol to 8 with ammonium hydroxide.

8.2 Ammonium hydroxide, concentrated (14N): Reagent grade.

8.3 Ammonium hydroxide, (1.4N): Add 100 ml concentrated ammonium hydroxide to 800 ml distilled water. Cool and dilute to 1000 ml.

8.4 Ammonium hydroxide, (0.7N): Add 50 ml concentrated ammonium hydroxide to 900 ml distilled water. Cool and dilute to 1000 ml.

8.5 Ammonium hydroxide-ammonium nitrate solution (0.10N NH_4OH-0.10N NH_4NO_3): Dissolve 8.0 g of reagent grade ammonium nitrate in 500 ml distilled water. Add 7 ml of reagent grade, concentrated ammonium hydroxide and dilute to 1000 ml.

8.6 Boric acid, powder: Reagent grade.

8.7 Calcium chloride (2N): Dissolve 111 g of calcium chloride ($CaCl_2$) in 900 ml distilled water. Cool and dilute to 1000 ml.

8.8 Dichromate cleaning solution: Dissolve 50 g sodium dichromate in 25 ml of water. Cautiously add concentrated sulfuric acid (a few drops at a time) until further additions cause little reaction. Make up to 1000 ml with concentrated sulfuric acid.

8.9 Ferric chloride 0.3N (5.6 mg Fe/ml): Dissolve 27 g of reagent grade ferric chloride ($FeCl_3 6H_2O$) in 300 ml of 6N hydrochloric acid. Dilute to 1000 ml with distilled water.

8.10 Hydriodic acid, concentrated (50%): Reagent grade.

8.11 Hydrobromic acid, concentrated (49%): Reagent grade.

8.12 Hydrochloric acid, concentrated (12N): Reagent grade.

8.13 Hydrochloric acid, 9N: Add 750 ml concentrated hydrochloric acid to 200 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.14 Hydrochloric acid, 6N: Add 500 ml concentrated hydrochloric acid to 450 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.15 Hydrochloric acid, 1.2N: Add 100 ml concentrated hydrochloric acid to 850 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.16 Hydrofluoric acid, concentrated (48%): Reagent grade.

8.17 Hydrogen peroxide, concentrated (30%): Reagent grade.

8.18 Ion exchange (anion) resin, Bio-Rad AG 1-X2, chloride form, 50-100 mesh.

8.19 Nitric acid, concentrated (16N): Reagent grade.

8.20 Nitric acid, 7.2N: Slowly add 455 ml concentrated nitric acid to 500 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.21 Nitric acid, 4N: Slowly add 250 ml concentrated nitric acid to 800 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.22 Potassium fluoride, anhydrous, granular: Reagent grade.

8.23 Silica sand, spherical grained, 60-200 mesh (must be free of radiochemical contaminants).

8.24 Sodium bisulfite, powder: Reagent grade.

8.25 Sodium hydroxide, pellets: Reagent grade.

8.26 Sodium hydroxide, 12.5N: Dissolve 100 g sodium hydroxide pellets in 150 ml distilled water. Cool, then adjust volume to 200 ml.

8.27 Sulfuric acid, concentrated (36N): Reagent grade.

8.28 Sulfuric acid, 3.6N: With caution, add 100 ml concentrated sulfuric acid to 850 ml distilled water. Cool, then adjust the volume to 1000 ml with distilled water.

8.29 Sulfuric acid, 0.36N: With caution, add 10 ml concentrated sulfuric acid to 900 ml distilled water. Adjust to 1000 ml with distilled water.

8.30 Thymol blue indicator, 0.02%: Dissolve 0.02 g thymol blue in 10 ml ethanol. Dilute to 100 ml with distilled water.

8.31 Tracer solutions: Purified and calibrated solutions of plutonium-236 (∿5 pCi/ml), uranium-232 (∿5 pCi/ml), and thorium-234 (∿100 pCi/ml) dissolved in 4N nitric acid.

9. Apparatus

9.1 Alpha spectrometric analyzer: A counting system consisting of a multichannel analyzer, biasing electronics, a printer, a vacuum pump and silicon surface barrier detectors operated in vacuum chambers.

9.2 Blast burner: Adjustable. High temperature.

9.3 Caps: Black resin, poly-seal liner, 22 mm, GCMI 400-thread design.

9.4 Centrifuge: 50-ml, 250-ml, and 500-ml capacity.

9.5 Centrifuge bottles: 50 ml plastic disposable, 250 ml Pyrex, 500 ml Pyrex.

9.6 Chromatographic column: A 250-mm by 14.5-mm i.d. tube with a 250-ml reservoir, and a stopcock with a Teflon plug, a course fritted glass disc is fused in the tube just above the stopcock to support the resin.

9.7 Electrolysis apparatus: 10-volt, 5-amp capacity.

9.8 Muffle furnace: Capable of reaching 750°C.

9.9 Neoprene sheet: 0.079-cm (1/32-inch) thickness.

9.10 Platinum or platinum-iridium anode: 1.27-cm (1/2-inch) diameter, 0.08-cm (1/32-inch) platinum or platinum-iridium disk having six 0.32-cm (1/8-inch) perforations and attached at the center to a 10-cm (4-inch) length of 0.16-cm (1/16-inch) platinum or platinum-iridium rod.

9.11 Rivets: #BS-4830 Dot Speedy rivets, solid brass, Carr Fastener Company, Cambridge, Massachusetts.

9.12 Stainless steel disks: 1.91-cm (3/4-inch) diameter, 0.38-mm (15-mil) thick, type 304 stainless steel planchets pre-polished to a mirror finish.

9.13 Teflon beakers and covers: Griffin, Chemware, 100 ml, 250 ml, and 500 ml.

9.14 Vials: Polyethylene, 25-ml screw cap, Packard #6001075.

10. Procedure

10.1 Sample Preparation

ANIMAL TISSUE ASH AND VEGETATION ASH

10.1.1 Transfer 10 g of previously ground and homogenized ash into a 250-ml graduated borosilicate beaker. Add 1 ml each of the appropriate tracers, (plutonium-236, uranium-232, or thorium-234) and 40 ml concentrated nitric acid. Cover and boil until it evaporates to dryness.

10.1.2 Wet the residue with concentrated nitric acid with intervening evaporations until a light-colored residue is obtained, then allow the nitric acid to evaporate. (If the residue is a porous black char following step 10.1.1, it will speed matters to ignite the sample in a muffle overnight at 600-700^{o} C before proceeding with the nitric acid digestion in 10.1.2.)

10.1.3 Transfer the residue to a 100-ml Teflon beaker using concentrated nitric acid. Evaporate twice with intervening additions of 10 ml of concentrated nitric acid and 15 ml of 48% hydrofluoric acid.

10.1.4 Evaporate the contents of the Teflon beaker to dryness. Add 10 ml 6N hydrochloric acid, evaporate to dryness, then dissolve the residue in 50 ml 6N hydrochloric acid. Transfer the solution to a 1000-ml Pyrex beaker rinsing with 6N hydrochloric acid.

10.1.5 Dilute the solution to 600 ml with 6N hydrochloric acid. Add 20 ml 2N calcium chloride and heat to the boiling point. While stirring, add concentrated ammonium hydroxide until precipitation begins and then add 40 ml in excess. Set the beaker aside to cool.

10.1.6 Remove the supernatant liquid by aspiration, and transfer the remaining slurry to a 500-ml centrifuge bottle. Centrifuge and discard the supernatant liquid. Dissolve the precipitate with a volume of 12N hydrochloric acid equal to that of the precipitate.

10.1.7 Transfer the solution to a 150-ml graduated borosilicate beaker and dilute to 60 ml with 6N hydrochloric acid. Continue to step 10.3.2 of the separation procedure.

BONE ASH

10.1.8 Weigh 1 g ash into a tared 100-ml Teflon beaker. Add 60 ml 6N hydrochloric acid, a few drops 30% hydrogen peroxide, and 1 ml each of the appropriate tracer solutions. Cover and digest overnight on a hot plate.

10.1.9 Transfer the solution to a 50-ml centrifuge tube using 6N hydrochloric acid and centrifuge. Pour the supernatant liquid into a 150-ml graduated borosilicate beaker and set aside. Return the residue to the Teflon beaker using 10 ml 48% hydrofluoric acid and 5 ml concentrated nitric acid. Evaporate this solution to dryness.

10.1.10 Wet the residue with 30% hydrogen peroxide and evaporate to dryness. Add 10 ml 6N hydrochloric acid and evaporate to dryness. Add 5 ml 6N hydrochloric acid and one drop 30% hydrogen peroxide. Heat to dissolve the residue and add the solution to the supernatant liquid in the glass beaker.

10.1.11 Adjust the combined liquid volume to 60 ml by evaporation or by addition of 6N hydrochloric acid. Proceed to step 10.3.2 of the separation procedure.

GLASS-FIBER FILTERS

10.1.12 Place filter or filters in a 400-ml Teflon beaker, 250-ml platinum dish. Add appropriate tracers (1 ml each), then wet the sample with concentrated nitric acid. Add 10 ml 48% hydrofluoric acid and evaporate on a hot plate to dryness.

10.1.13 Repeat acid additions and evaporations until the silica has been volatilized.

10.1.14 Add 30 ml concentrated nitric acid and again evaporate to dryness. Repeat.

10.1.15 Add 30 ml concentrated nitric acid, 5 g boric acid and 1 ml 0.3N ferric chloride. Evaporate to approximately 10 ml.

10.1.16 Dilute to 100 ml with distilled water and heat to dissolve salts.

10.1.17 Add 12.5N sodium hydroxide until precipitation ceases (pH 9), then add 15 g sodium hydroxide pellets. Cover and boil for 1 to 2 hours on a hot plate.

10.1.18 Continue at step 10.1.24 of the soil preparation.

SOIL

10.1.19 Weigh 10 g of soil, which has been previously ground to 100 mesh, into a porcelain crucible. Heat overnight at 700° C. Cool and transfer to a 200-ml Teflon beaker. Add 1 ml each of the tracers plus 1 ml 0.3N ferric chloride. Cautiously add 60 ml 16N nitric acid and 30 ml 48% hydrofluoric acid, allowing time between additions for foaming to subside. Cover with a Teflon lid and digest on a 400° C hot plate for 1 to 2 hours. Never let volume go below 20 ml.

10.1.20 Remove from the hot plate and cool slightly before adding 30 ml each of 16N nitric acid and 48% hydrofluoric acid. Digest without the lid with intermittent stirring for 1 hour.

10.1.21 Cool, then carefully add 20 ml concentrated hydrochloric acid with stirring. Digest on the hot plate for 45 minutes.

10.1.22 With stirring, add 5 g of boric acid powder. After 15 minutes digestion, add 0.2 g of sodium bisulfite crystals and continue heating until the volume is reduced to approximately 20 ml.

10.1.23 Dilute to 50 ml with distilled water. Add 50% sodium hydroxide solution until precipitation ceases (pH 9), then add 15 g of sodium hydroxide pellets. Cover and boil for 1 to 2 hours on a hot plate.

10.1.24 Transfer the solution and precipitate to a 500-ml Pyrex centrifuge bottle using distilled water. Centrifuge for at least 15 minutes at 1500 rpm. Decant and discard the supernate. Add approximately 10 ml concentrated nitric acid to the original Teflon beaker, cover, and reflux on the hot plate to dissolve any remaining residue.

10.1.25 Add approximately 1 g boric acid to the centrifuge bottle and stir the mixture with a stream of distilled water from a wash bottle. Add the nitric acid from the Teflon beaker, rinsing with distilled water. Rinse the beaker with an additional 10 ml concentrated nitric acid and add to the bottle. Warm on a hot plate for a few minutes to complete the dissolution.

10.1.26 Add 200 ml of distilled water and adjust the pH to 9 with 14N ammonium hydroxide. Adjust the volume to 450 ml and centrifuge at 1500 rpm for 15 minutes. Decant and discard supernate.

10.1.27 Dissolve the precipitate with a minimum of concentrated hydrochloric acid. Warm on a hot plate to speed dissolution. Transfer back to the Teflon beaker with approximately 30 ml of distilled water. Add 50% sodium hydroxide until precipitation ceases, then add 15 g sodium hydroxide pellets. Cover and boil for 1 hour.

10.1.28 Transfer the solution and precipitate back to the centrifuge bottle with distilled water. Adjust the volume to 450 ml and centrifuge for 15 minutes at 1500 rpm. Decant and discard supernate. Add 10 ml concentrated hydrochloric acid to the Teflon beaker, cover, and reflux on the hot plate for a few minutes.

10.1.29 Transfer the hydrochloric acid from the Teflon beaker to the centrifuge bottle, rinsing with distilled water. Rinse the beaker with an additional 10 ml concentrated hydrochloric acid and add to the bottle. Warm on a hot plate to aid dissolution.

10.1.30 Add 200 ml of distilled water, then adjust the pH to 9 with concentrated amonium hydroxide. Increase the volume to 450 ml with distilled water then centrifuge at 1500 rpm for 15 minutes. Discard supernate.

10.1.31 Add a minimum volume of concentrated hydrochloric acid to the precipitate. Swirl to dissolve the precipitate, then transfer to a graduated 150-ml beaker rinsing with 6N hydrochloric acid. Adjust the solution volume to 40 ml with 6N hydrochloric acid and proceed with step (10.3.2) of the separation procedure.

URINE

10.1.32 Measure the sample volume with a graduated cylinder and transfer it into a beaker with a capacity approximately 50% larger than the sample. Rinse the sample container with concentrated hydrochloric acid, using 40 ml of acid per liter of sample. Add this rinse to the sample. Rinse the container again with 60 ml of concentrated nitric acid. Set aside this rinse for later use.

10.1.33 Add the appropriate tracers, 10 ml 2N calcium chloride, and a volume of 30% hydrogen peroxide equal to the volume of concentrated hydrochloric acid used in the previous step. Place a Teflon stirring rod in the beaker and heat to the boiling point. When foaming subsides, cover the beaker and allow the solution to simmer for 1 hour.

10.1.34 Add the concentrated nitric acid rinse to the beaker and continue to simmer for another hour.

10.1.35 While stirring the hot solution, add concentrated ammonium hydroxide slowly until precipitation begins and then add an excess equal to 60 ml of ammonium hydroxide per liter of original sample. Cover the beaker and set aside to cool.

10.1.36 Remove the supernatant liquid by aspiration and discard. Transfer the remaining slurry into a 50-ml plastic centrifuge tube using 0.7N ammonium hydroxide. Centrifuge and discard the supernate.

10.1.37 Rinse the sample beaker with approximately 10 ml of concentrated nitric acid and transfer to the residue in the centrifuge tube. Shake to dissolve the precipitate, then transfer the solution to a 250-ml beaker using about 5 ml of concentrated nitric acid as a rinse. Cover the beaker with a watch glass and boil on a hot plate until the residue is dry.

10.1.38 Wet the residue alternately with 30% hydrogen peroxide and concentrated nitric acid with intervening evaporations until a white ash is obtained and then allow all of the nitric acid to evaporate.

10.1.39 Add 50 ml 6N hydrochloric acid and boil until the volume is reduced to 25 ml. Add 6N hydrochloric acid to increase the volume to 50 ml. Proceed at step (10.3.2) of the separation procedure.

WATER

10.1.40 Add appropriate tracers, 5 ml 0.3N ferric chloride, and 20 ml of 30% hydrogen peroxide to 1 liter of sample, previously preserved by the addition of 20 ml concentrated nitric acid per gallon of water. Simmer until the hydrogen peroxide has decomposed.

10.1.41 While stirring, add concentrated ammonium hydroxide to the hot solution until precipitation begins and then add 15 ml in excess. Continue heating until the precipitate has coagulated, then allow to cool.

10.1.42 Remove the supernatant liquid by aspiration and transfer the precipitate to a centrifuge tube using 0.7N ammonium hydroxide. Add approximately 10 ml of concentrated nitric acid to the beaker, cover, and reflux on the hot plate to dissolve any remaining residue. Cool and set aside.

10.1.43 Dissolve the precipitate in the centrifuge tube by adding a volume of concentrated hydrochloric acid equal to the volume of the precipitate. Centrifuge and decant the supernate into a 150-ml Pyrex beaker.

10.1.44 Using a minimum of concentrated nitric acid, transfer any insoluble residue from the tube to a 100-ml Teflon beaker. Add the nitric acid solution from the original beaker in step (10.1.42) and evaporate to dryness on the hot plate.

10.1.45 Add 10 ml 48% hydrofluoric acid and 5 ml concentrated nitric acid. Evaporate to dryness. If any organic material remains, wet the residue with 30% hydrogen peroxide and evaporate to dryness.

10.1.46 Add 10 ml 6N hydrochloric acid and evaporate to dryness. Add 5 ml 6N hydrochloric acid and one drop 30% hydrogen peroxide. Heat to dissolve the residue and add the solution to the supernatant liquid from step (10.1.43). Evaporate the combined solutions to 60 ml and continue with step (10.3.2).

10.2 Ion Exchange Column Preparation

10.2.1 Remove fines from the resin by repeated suspension in distilled water and decantation. Add concentrated hydrochloric acid equal to 10% of the volume of slurry to shrink the resin. Transfer the resin to the column in slurry form to give a settled resin bed of 20 ml volume. Add dry 60 to 200 mesh silica sand to a depth of 15 mm through a layer of 1.2N hydrochloric acid. The sand prevents resuspension of the resin and, by its capillarity, stops the flow between additions of reagents enabling unattended operation.

10.3 Ion Exchange Separations

10.3.1 Immediately prior to use, condition the ion exchange column with 100 ml of 9N hydrochloric acid containing a drop of 30% hydrogen peroxide at a flow rate of 6 ml/min.

10.3.2 Add a volume of 12N hydrochloric acid to the sample that is equal to the volume of the 6N solution to adjust the acid concentration to 9N. Add one drop 30% hydrogen peroxide for each 10 ml of 9N solution, cover with a watch glass, and heat the solution to 80-90° C for 1 hour. Cool to room temperature.

10.3.3 Transfer the sample to the column reservoir using 9N hydrochloric acid as a rinse. If barium chloride, sodium chloride, or other solid matter is present, filter the solution into the reservoir through a plug of glass wool in the stem of a funnel.

10.3.4 Pass the 9N sample solution through the column at a flow rate of 3 ml/min. Flush the reservoir three times with 15-ml volumes of 9N hydrochloric acid and drain each rinse at 3 ml/min. Combine and save the 9N eluates for thorium analysis.

10.3.5 Wash the column with an additional 50 ml 9N hydrochloric acid containing one drop of 30% hydrogen peroxide. Elute at 3 ml/min and discard eluate. If plutonium analysis is not required, proceed to step 10.3.8.

PLUTONIUM

10.3.6 Elute plutonium from the column using 25 ml 49% hydrobromic acid at 3 ml/min. Collect the eluate in a 100-ml Pyrex beaker. Wash the column with an additional 50 ml 49% hydrobromic acid and combine with the 25-ml eluate.

10.3.7 Add 0.5 ml of concentrated sulfuric acid to the sample solution and evaporate at low heat to fumes of sulfuric acid. Add two drops of 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Save this fraction for electrodeposition of plutonium, step (10.4.12).

URANIUM

10.3.8 Remove iron from the column with a fresh solution prepared by mixing 109 ml of 12N hydrochloric acid with 31 ml of distilled water and 50 ml of 50% hydriodic acid. Rinse the column reservoir three times with 15-ml portions of this solution and elute at 3 ml/min. Add an additional 100 ml of the solution and elute at the same rate. Discard the eluates.

10.3.9 Rinse the column with two 15-ml portions of 9N hydrochloric acid followed by 5 ml 1.2N hydrochloric acid to remove residual hydriodic acid. Discard the eluates.

10.3.10 Elute uranium with 50 ml 1.2N hydrochloric acid at 3 ml/min. Collect the eluate in a 100-ml glass beaker. Add 0.5 ml concentrated sulfuric acid to the beaker and evaporate to fumes of sulfuric acid. Add 5 drops 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Save for electrodeposition of uranium, step (10.4.12).

THORIUM

10.3.11 To prepare the column for thorium, add 100 ml 1.2N hydrochloric acid to the column reservoir and elute at 3 ml/min. Discard the eluate. Add 150 ml 7.2N nitric acid and elute at 3 ml/min. Discard the eluate.

10.3.12 Evaporate the combined 9N thorium eluates (from step 10.3.4) to dryness on a hot plate. Dissolve the residue with 20 ml 7.2N nitric acid, plus 5 drops of 30% hydrogen peroxide. Cover and reflux for 45 minutes on the hot plate. Add 3 more drops 30% hydrogen peroxide and continue to heat for 15 minutes. Cool to room temperature.

10.3.13 Transfer the solution to the column reservoir, rinsing the beaker with a minimum of 7.2N nitric acid. Elute at 3 ml/min and discard the eluate. Rinse the reservoir with three 10-ml portions 7.2N nitric acid and drain at the same rate. Wash the column with 100 ml 7.2N nitric acid and discard eluate.

10.3.14 Rinse the reservoir with 5 ml 9N hydrochloric acid and drain at 3 ml/min. Discard the eluate. Elute the thorium with 100 ml 9N hydrochloric acid at 3 ml/min and collect the eluate in a 150-ml glass beaker.

Add 0.5 ml concentrated sulfuric acid to the beaker and evaporate to sulfuric acid fumes. Add 5 drops 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Continue with the electrodeposition of thorium at step (10.4.12).

10.4 Electrodeposition

CONSTRUCTION OF ELECTRODEPOSITION CELLS

10.4.1 Cut a 1.43-cm (9/16-inch) hole in the bottom of the polyethylene vial with a sharp cork borer. Improve the seal by abrading the threaded end with wet #320 waterproof emery paper held against a flat surface. Finish with wet #600 emery paper.

10.4.2 Remove the polyethylene liner from a 22-mm Poly-Seal cap. With a cork borer or leather punch, cut out the polyethylene tube from the liner. The conical part of the liner is used as a cover for the cell to minimize escape of spray.

10.4.3 Drill a 0.355-cm (0.140-inch, #28 drill) hole through the center of the cap. Bevel the edge of the hole on the inside of the cap with a reamer.

10.4.4 Cut a 1.91-cm (3/4-inch) disc from 0.079-cm neoprene sheeting with a cork borer or a die. Cut a 0.317-cm (1/8-inch) hole in the center of the disc with a cork borer or leather punch.

10.4.5 Place the washer in the cap and pass the shank of the rivet through the washer and the hole in the cap.

CLEANING

10.4.6 Remove any surface film of oil from the polyethylene body of the cell with acetone followed by water.

10.4.7 Completely immerse the body of the cell in dichromate-sulfuric acid cleaning solution for 2 to 3 hours. Rinse off the cleaning solution with water and immerse the cell in 4N nitric acid for at least 1 hour. Rinse and immerse in distilled water until ready to use.

10.4.8 The cleaning process renders the polyethylene hydrophilic, provided the cell is kept continuously wet after having been cleaned. The polyethylene parts of used cells can be rinsed and then cleaned by the directions given in 10.4.7 except that the immersion in dichromate sulfuric acid cleaning solution is limited to 1 hour. Clean the caps and neoprene washers by immersing for a few minutes in 4N nitric acid and then rinse with water.

ASSEMBLY

10.4.9 Connect one hole of a 2-hole #6 rubber stopper to an aspirator pump with a length of rubber tubing.

10.4.10 Rinse the polyethylene cell with distilled water but do not dry. Hold the planchet centered against the threaded end of the cell and place the rubber stopper against the other end of the cell. Apply suction by placing a finger over the open hole of the stopper. The vacuum will hold the planchet in a centered position while the cap assembly is screwed on. Fill the cell halfway with water and alternately apply and release the vacuum. The flexing will cause the planchet to seat more firmly against the cell. Check to see that no stream of air bubbles rises through the water when vacuum is applied. If the vacuum is great enough, the water may boil, but the boiling is easily distinguished from air leakage.

10.4.11 Fill the assembled cell to the top with water to preserve the hydrophilic character of the cell until ready to add sample.

ELECTRODEPOSITION

10.4.12 Add 3 ml of water to the cool sulfuric acid sample solution. Replace the watch glass and warm the solution for a minute or two on a hot plate and then allow to cool.

10.4.13 Add 4 drops 0.02% thymol blue sodium salt. Neutralize the solution to the salmon-pink endpoint (pH 2) by blowing gaseous ammonia over the surface while swirling the solution. The gaseous ammonia is obtained from a polyethylene wash bottle having the inner portion of the delivery tube removed and containing concentrated ammonium hydroxide. If the endpoint is overstepped to a yellow color, add 3.6N sulfuric acid, a drop at a time, until the solution turns pink.

10.4.14 Pour the neutralized solution into the plating cell. Draw 6 ml 3.6N sulfuric acid into a pipette and use this in small increments to rinse the beaker three or more times. Add the rinses to the cell.

10.4.15 Neutralize the solution again to pH 2 with gaseous ammonia. The solution should have a straw color when viewed from the top and a slight pinkish cast when viewed through the sides of the cell. If the endpoint is overstepped, use 3.6N sulfuric acid, a drop at a time, to return the solution to the proper color.

10.4.16 Lower the platinum anode into the solution until the bottom edge of the anode is about 2 mm above the shoulder of the cell. If set too deep, gas bubbles will be trapped and cause fluctuation of the current. When the current is first turned on, it will be about 0.8 ampere. As the solution warms, the current will increase and must be readjusted to 1.2 amperes when it rises above this value. After 15 to 30 minutes, the current will stabilize and electrolysis can be allowed to continue at 1.2 ampere without attention for a total electrolysis time of 1.5 to 2 hours.

10.4.17 With current on, add 10 ml of 10% ammonium hydroxide and continue the electrolysis for 1 minute. Lift the anode out of the cell and then switch off the current. Pour the solution out of the cell and rapidly flood the cell three times with 0.1N ammonium nitrate 0.1N ammonium hydroxide solution. Disassemble the cell and quickly wash the planchet with a stream

of alkaline ethyl alcohol. Touch a piece of filter paper to the edge of the planchet to adsorb the film of alcohol.

10.4.18 Place the disc in a cupped planchet and heat for 10 minutes on a hot plate. Cool and count the sample for 1000 minutes by alpha spectrometry.

11. Calibration

APPARATUS AND SUPPLIES

11.1 Windowless 2π gas flow proportional counter.

11.2 National Bureau of Standards (NBS) americium-241 point source, approximately 2×10^5 dpm deposited on platinum and certified to ± 1% of its stated activity.

11.3 Stainless steel discs, 2-inch diameter; mirror finish.

CALIBRATION OF THE 2π COUNTER

11.4 Refer to manufacturer's procedure manual for calibration procedures.

11.5 Determine the counting efficiency of the 2π counter by counting the NBS americium-241 standard. Accumulate approximately 5×10^5 counts. Calculate the counting efficiency by dividing the counts per minute by the certified disintegration rate (dpm).

11.6 Correct the counting efficiency for the difference in backscatter between platinum and stainless by dividing the calculated efficiency above by 1.023.

STANDARDIZATION OF TRACERS

11.7 All tracers are checked for non-isotopic alpha-emitting contaminants by electrodeposition and alpha spectrometry. If non-isotopic contaminants are found or known to be present, the tracer must be purified before standardization (Sill, 1974).

11.8 Transfer a 100- to 250-µl aliquot of the isotopically pure stock tracer (∿500 pCi/ml in a 2N nitric acid) to each of three 5-cm (2-inch) stainless steel planchets.

11.9 Allow the solutions to evaporate to complete dryness at room temperature.

11.10 Heat each planchet over a blast burner just to the first dull red glow. Then quickly lower the temperature by placing the planchet on a cold steel surface to minimize oxidation of the plate.

11.11 Count each planchet in the 2π counter, collecting at least 10^4 counts to ensure adequate statistical precision. Verify the 2π counter counting efficiency before and after counting.

11.12 Electrodeposit approximately 250 pCi of the isotopically pure tracer as described in sections 10.3.7 and 10.4.12.

11.13 Count the electroplated source on an alpha spectrometer for 100 minutes. Calculate the fraction of the total number of counts in the alpha spectrum that is due to the tracing nuclide ^{236}Pu or ^{243}Am. This fraction is the correction factor to be applied to the counting rates of the evaporated sources in the 2π counter.

11.14 Calculate the activity concentration of the tracer (pCi/ml) by multiplying the observed 2π counting rates of the evaporated sources by the correction factor (Step 11.13) and dividing by the 2π counter efficiency (Step 11.6) and 2.22 dpm/pCi.

CALIBRATION OF THE ALPHA SPECTROMETER

11.15 Because a point-source standard electrodeposited on platinum (the NBS americium-241 source) cannot be used to calibrate an alpha spectrometer for use with diffuse sources electrodeposited on stainless steel, a secondary standard must be employed.

11.16 Standardize a secondary source (such as one prepared in Step 11.12 or any alpha activity electrodeposited as described in Sections 10.3.7 and 10.4.12 through 10.4.18) by counting with the 2π counter until at least 10^4 counts have been collected.

11.17 Count the secondary source with the alpha spectrometer until at least 10^4 counts have been collected. Calculate the spectrometer efficiency by multiplying the source's counting rate on the spectrometer (summed over the entire energy range) by the 2π counting efficiency and dividing by the source's counting rate on the 2π counter.

12. Quality Control

Approximately 10% of all samples are recycled as blind duplicates. The results are evaluated by standard statistical tests, and corrective action is taken, if necessary.

Data obtained from efficiency determinations are plotted on line graphs to indicate the condition of the detectors and various electronic components.

13. Calculations

CALCULATION OF SAMPLE ACTIVITY (R)

13.1

$$\text{(R) isotope activity (pCi/unit)} = \frac{(A - A_1) \times F \times D)}{(B - B_1) \times \text{(sample size)}}$$

CALCULATION OF THE TWO-SIGMA ERROR (E)

13.2

$$(E) = 2R\sqrt{\frac{\frac{A}{T_s} + \frac{A_1}{T_B}}{(A - A_1)^2} + \frac{\frac{B}{T_s} + \frac{B_1}{T_B}}{(B - B_1)^2}}$$

where:

- A = gross sample counts per minute which appear in the alpha energy region characteristic of the specific nuclide being analyzed
- A_1 = background counts per minute in the same alpha energy region (channels) as "A" above
- B = gross tracer counts per minute from the sample disc
- B_1 = background counts per minute in the same alpha energy region (channels) as "B" above
- F = tracer activity in picocuries added to the sample
- D = fractional decay of the tracer between the time of its standardization and the time of the sample count
- T_s = sample counting time in minutes
- T_B = reagent blank (background) counting time in minutes

14. References

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ANALYSIS OF POLONIUM-210 IN SOIL AND AIR FILTERS

1. Principle

1.1 Samples are decomposed by digestion with hydrofluoric acid and nitric acid in the presence of lead carrier and a polonium-208 tracer. Polonium is co-precipitated with lead sulfide from a dilute acid solution separating it from calcium, iron and other interferences. The sulfide precipitate is dissolved in dilute hydrochloric acid and polonium is spontaneously deposited on a nickel disk. Polonium-210 and the polonium-208 tracer are measured by alpha spectrometry.

2. Application

2.1 This method is appropriate for the analysis of up to 1 gram of soil or one 10-cm (4-inch) diameter glass-fiber air filter.

3. Range

3.1 This method is designed to detect environmental levels of activity approaching 0.02 picocurie per sample. To avoid possible cross-contamination and contamination of the alpha detectors, sample activities should be limited to 25 picocuries or less.

4. Interferences

4.1 Samples containing extremely high levels of polonium-210 will result in invalid analyses by interfering with the determination of the polonium-208 tracer recovery. Samples should be screened by gross alpha counting to determine the proper sample aliquot.

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.

$$LLD = \frac{3.29\ S_o}{2.22 \times E \times S}$$

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

where 3.29 = $K_\alpha + K_\beta$

K_α = the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present (α) = 0.05

K_β = corresponding value for the predetermined degree of confidence for detecting the presence of activity ($1-\beta$) = 0.95

S_o = estimated standard error for the net sample activity

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

5.2 The sensitivity for an analysis is proportional to the actinide yield, the counter efficiency, and the length of alpha count. The sensitivity for an analysis having a 100% yield and employing a 1000-minute count on a counter having a counting efficiency of 0.20 cpm/dpm is 440 counts/picocurie.

6. Precision and accuracy

7. Shipment and storage of samples and sample stability

7.1 Samples should be analyzed as soon as possible after collection to avoid appreciable decay or ingrowth of the relatively short-lived polonium-210 in the sample, depending on its state of equilibrium, with its parent lead-210.

8. Reagents

8.1 Ammonium hydroxide, concentrated (14N): Reagent grade.

8.2 Ammonium hydroxide, (1.4N): With stirring, add 100 ml concentrated ammonium hydroxide to 800 ml of distilled water. Dilute to 1000 ml.

8.3 Citric acid, (40% w/v): Dissolve 40 g of reagent grade citric acid in 100 ml of distilled water.

8.4 Ethyl alcohol, (95%): Reagent grade.

8.5 Hydrochloric acid, concentrated (12N): Reagent grade.

8.6 Hydrochloric acid, (0.5N): Add 42 ml of 12N reagent grade, hydrochloric acid to 900 ml of distilled water. Dilute to 1000 ml with distilled water.

8.7 Hydrofluoric acid, concentrated (48%): Reagent grade.

8.8 Hydroxylamine hydrochloride (50% w/v): Dissolve 100 g of reagent grade hydroxylamine hydrochloride in 100 ml of distilled water.

8.9 Lead carrier, (10 mg/ml): Dissolve 1 g of lead nitrate ($Pb(NO_3)_2$) in 100 ml 4N nitric acid.

8.10 Nitric acid, concentrated (16N): Reagent grade.

8.11 Polonium-208 tracer: 5 pCi/ml in 4N nitric acid.

8.12 Thioacetamide, (10% w/v): Dissolve 50 g of reagent grade thioacetamide in 500 ml of distilled water.

9. Apparatus

9.1 Alpha spectrometric analyzer: A counting system consisting of a multichannel analyzer, biasing electronics, a printer, a vacuum pump and silicon surface barrier detectors operated in vacuum chambers.

9.2 Caps: Black resin, Poly-Seal liner, 22-mm GCMI thread design.

9.3 Centrifuge tubes: 50-ml, disposable.

9.4 Centrifuge

9.5 Deposition cells with 1.91-cm (3/4-inch) polished nickel disks.

9.5.1 Cut a 1.43-cm (9/16-inch) hole in the bottom of the polyethylene vial with a sharp cork borer. Improve the seal by abrading the threaded end with wet #320 waterproof emery paper held against a flat surface. Finish with wet #600 emery paper.

9.5.2 Remove the polyethylene liner from a 22-mm Poly-Seal cap.

9.5.3 Cut a 1.91-cm (3/4-inch) disc from 0.079-cm neoprene sheeting with a cork borer or a die. Place the disc in the cap.

9.5.4 Cleaning

9.5.5 Completely immerse the body of the cell in dichromate-sulfuric acid cleaning solution for 2 to 3 hours. Rinse off the cleaning solution with water and immerse the cell in 4N nitric acid for at least one hour. Rinse and immerse in distilled water until ready to use.

9.5.6 The cleaning process renders the polyethylene hydrophilic, provided the cell is kept continuously wet after having been cleaned. The polyethylene parts of used cells can be rinsed and then cleaned by the directions given in 9.5.5, except that the immersion in dichromate sulfuric acid cleaning solution is limited to one hour. Clean the caps and neoprene washers by immersing for a few minutes in 4N nitric acid and then rinse with water.

9.5.7 Assembly

Connect one hole of a 2-hole #6 rubber stopper to an aspirator pump with a length of rubber tubing.

9.5.8 Rinse the polyethylene cell with distilled water but do not dry. Hold the nickel disc centered against the threaded end of the cell and place the rubber stopper against the other end of the cell. Apply suction by placing a finger over the open hole of the stopper. The vacuum will hold the planchet in a centered position while the cap assembly is screwed on. Fill the cell halfway with water and alternately apply and release the vacuum. The flexing will cause the planchet to seat more firmly against the cell.

9.5.9 Check to see that no stream of air bubbles rises through the water when vacuum is applied. If the vacuum is great enough, the water may boil, but the boiling is easily distinguished from air leakage.

9.5.10 Fill the assembled cell to the top with water to preserve the hydrophilic character of the cell until ready to add sample.

9.6 Neoprene sheet: 0.079-cm (1/32-inch) thickness.

9.7 pH meter.

9.8 Steam or hot water bath.

9.9 Stirrer.

9.10 Teflon beakers: 100-ml.

9.11 Vials: Polyethylene, 25-ml screw cap, Packard #6001075.

10. Procedure

10.1 Weigh and transfer 0.5 to 1.0 grams dried soil, or a 10-cm (4-inch) diameter air filter, into a 100-ml Teflon beaker. Keep filter as flat and close to bottom as possible. Add 1 ml polonium tracer and 1 ml lead carrier.

10.2 Add 10 ml concentrated nitric acid and 10 ml 48% hydrofluoric acid and place on hot plate. Evaporate to dryness without bringing to a boil. Repeat 3 more times.

10.3 Add 10 ml concentrated nitric acid and evaporate to dryness. Repeat 2 more times.

10.4 Add enough concentrated nitric acid and heat to dissolve salts. Add 10 ml water and filter through a Whatman #42 filter, using a disposable funnel into a disposable 50-ml centrifuge tube. Wash filter with 10 ml water followed by 10 ml 0.05N hydrochloric acid.

10.5 Evaporate the solution in the centrifuge tube to dryness in a steam bath. Redissolve with 1 ml concentrated hydrochloric acid. Add 10 ml water and adjust pH to 3.5-4.0 with 0.5N hydrochloric acid and/or 1.4N ammonium hydroxide.

10.6 Add 5 ml of 10% thioacetamide solution and digest for 1 to 2 hours on the steam bath. Cool. Centrifuge. Decant and discard the supernatant liquid.

10.7 Dissolve the precipitate with 1 ml concentrated hydrochloric acid. Repeat steps 10.5 and 10.6.

10.8 Dissolve the residue with 1 ml concentrated hydrochloric acid while heating on the steam bath. Add 5 ml water and filter through a Whatman #42 filter (using a disposable funnel) into a new 50-ml disposable centri-

fuge tube. Wash the filter with 1 ml water and 1 ml 0.5N hydrochloric acid.

10.9 Transfer to a deposition cell with a minimum of water and add 2 ml 40% citric acid solution and 2 ml hydroxamine hydrochloride. Add water until cell is 3/4 full. Place cell in a hot water bath at 80° C and stir for 1 to 1 1/2 hours to plate the polonium.

10.10 Remove the cell from the hot water bath and discard the solution.

10.11 Wash the deposition cell with distilled water and then with ethyl alcohol.

10.12 Heat the disc (in an aluminum planchet) on a hot plate (200° C to 250° C) for 20 minutes. Cool and count in an alpha spectrometer.

11. Calibration

11.1 Calibration of the polonium-208 tracer is performed by co-deposition with standardized polonium-210 solutions and by liquid scintillation counting.

12. Quality Control

13. Calculations

CALCULATION OF SAMPLE ACTIVITY (R)

13.1

$$\text{(R) isotope activity (pCi/unit)} = \frac{(A - A_1) \times F \times D)}{(B - B_1) \times \text{(sample size)}}$$

CALCULATION OF THE TWO SIGMA ERROR (E)

13.2

$$(E) = 2R\sqrt{\frac{\frac{A}{T_s} + \frac{A_1}{T_B}}{(A - A_1)^2} + \frac{\frac{B}{T_s} + \frac{B_1}{T_B}}{(B - B_1)^2}}$$

where
- A = gross sample counts per minute which appear in the polonium-210 energy region
- A_1 = background counts per minute in the same alpha energy region (channels) as "A" above
- B = gross tracer counts per minute from the sample disc
- B_1 = background counts per minute in the same alpha energy region (channels) as "B" above
- F = tracer activity in picocuries added to the sample
- D = fractional decay of the tracer between the time of its standardization and the time of the sample count

T_S = sample counting time in minutes

T_B = background counting time in minutes

14. References

Figgins, P. E., Radiochemistry of Polonium. National Academy of Sciences--National Research Council. NAS-NS 3037. (1961)

Harley, J. H., HASL Procedures Manual. U.S. Atomic Energy Commission. HASL-300. (1972)

DETERMINATION OF STRONTIUM-89 AND STRONTIUM-90 IN MILK

1. Principle

1.1 Milk with added carriers and disodium ethylenediaminetetraacetate (Na_2 EDTA) is passed through a cation exchange resin. The alkali metals and most alkaline earths are adsorbed on the cation resin, and the complexed calcium passes through unabsorbed. The alkaline earth metals are removed from the cation resin by elution with a sodium chloride solution and precipitated as carbonates. Barium is removed by chromate precipitation. Strontium-89 and strontium-90 are determined by counting twice, once immediately after separation and again after yttrium-90 ingrowth. Chemical yield is determined gravimetrically.

2. Application

2.1 This method is applicable for the determination of strontium-89 and strontium-90 in raw, pasturized, and homogenized milk.

2.2 Strontium-89 and strontium-90 in sour milk may be determined by this method using the batch process described in 10.14.

3. Range

3.1 No range has been established.

4. Interferences

4.1 Cream in raw milk must be separated prior to passing the milk through the resin as it will coat the resin exchange sites. The cream may be removed without affecting results as the strontium is complexed only with the protein.

4.2 Other radionuclides usually present in milk do not interfere.

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.

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

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* 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 (α) = .05.

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

6.1 The expected precision for strontium-90, based on the 95% confidence level analytical error, is 3.0 pCi/l up to a concentration of 30 pCi/l and 10% above 30 pCi/l. The expected precision of strontium-89, based on the 95% confidence level analytical error, is 10 pCi/l up to a concentration of 100 pCi/l and 10% above 100 pCi/l. These precision values are those used in the duplicate analysis program and recommended by EMSL-LV Quality Assurance Branch.

7. Shipment and storage of samples and sample stability

7.1 Milk samples should be preserved with 15 ml of 37% formaldehyde solution. Refrigerated samples will be usable (as samples) for 10 to 12 weeks.

8. Reagents

8.1 Ammonium acetate buffer solution. pH 5.2: Dissolve 153 g ammonium acetate in 800 ml distilled water, and 28.6 ml glacial acetic acid. Adjust to pH 5.2 using either ammonium hydroxide or acetic acid. Dilute to 1000 ml with distilled water.

8.2 Ammonium hydroxide, concentrated: Reagent grade.

8.3 Ammonium hydroxide, 6N: Dilute 400 ml concentrated ammonium hydroxide to 1000 ml with distilled water.

8.4 Barium carrier, 40 mg/ml: Dissolve 76.2 g barium nitrate in 800 ml distilled water and dilute to 1000 ml.

8.5 Complexing solution: Dissolve 216 g disodium ethylenediaminetetraacetate in 250 ml water. Add 10 ml Sr^{2+} carrier (40 mg/ml, 10 ml Ba^{2+} carrier (40 mg/ml), and 200 ml ammonium acetate buffer (pH 5.2). Adjust the pH to 5.2 using approximately 70 ml 6N ammonium hydroxide; dilute to 3 liters with distilled water. Readjust pH to 5.2 before using.

8.6 Dowex 50W-X 8: 50-100 Mesh

8.7 Ethylenediaminetetraacetate disodium (Na_2 EDTA), 3%: Dissolve 33.3 g Na_2 EDTA in 900 ml distilled water; adjust pH to 5.2 with ammonium acetate buffer solution; dilute to 1000 ml with distilled water. Readjust pH to 5.2 just prior to use.

8.8 Nitric acid, concentrated: Reagent grade.

8.9 Nitric acid, 90%: Reagent grade.

8.10 Nitric acid, 1N; Add 62.5 ml concentrated nitric acid to 800 ml distilled water. Cool, and dilute to 1000 ml.

8.11 Sodium carbonate, 3N: Dissolve 159 g sodium carbonate in 800 ml distilled water and dilute to 1000 ml.

8.12 Sodium chloride, 4N: Dissolve 234 g sodium chloride in 800 ml distilled water and dilute to 1000 ml.

8.13 Sodium chloride, 1.5N; Dissolve 88 g sodium chloride in 800 ml distilled water and dilute to 1000 ml.

8.14 Sodium chromate, 1N: Dissolve 81 g sodium chromate in 800 ml distilled water and dilute to 1000 ml.

8.15 Sodium hydroxide, 6N: Dissolve 240 g sodium hydroxide in 800 ml water. Cool and dilute to 1000 ml.

8.16 Strontium carrier, 40 mg/ml: Dissolve 96.6 g strontium nitrate in 800 ml distilled water and dilute to 1000 ml.

9. Apparatus

9.1 Ion exchange columns (Figure 8)

9.2 Low background beta counter

10. Procedure

FRESH MILK

10.1 Add 300 ml EDTA complexing solution to 1 liter milk, filter through cheesecloth and mix well. Pour sample into funnel (Figure 8). Remove screw cap from bottom of cation column and allow milk to pass through at gravity flow (approximately 100 ml/min).

10.2 Wash resin with three 100-ml portions of hot distilled water, leaving enough water on columns to keep them wet. Attach stopcock assembly (Figure 8) to bottom of cation column. Add 800-ml hot (60° C) distilled water and allow to flow through the column at a rate of 100 ml/min.

10.3 Wash column with 800 ml 3% EDTA (pH 5.2) at a flow of 20 ml/min to remove residual calcium; then wash column with 200 ml distilled water.

10.4 Wash adsorbed EDTA from column with 200 ml 1.5N sodium chloride at 10 ml/min. Place 500 ml 4N sodium chloride in funnel and let it flow through column at rate of 20 ml/min.

10.5 Collect the first 400 ml of eluent at a flow rate of 20 ml/min in a 500-ml centrifuge bottle. See 10.13 to regenerate the resin.

10.6 Add 1 ml 6N sodium hydroxide to the 400-ml strontium-barium fraction, and with stirring add 10 ml 3N sodium carbonate. Continue stirring for 30 minutes. An occasional sample will not precipitate. Warming the solution with stirring will usually bring down the precipitate. Centrifuge, and discard supernate.

10.7 Dissolve precipitate with 5 ml 1N nitric acid and transfer to 40-ml centrifuge tube. Add 5 ml ammonium acetate buffer solution (pH 5.2). Adjust pH to 4.6 with concentrated ammonium hydroxide and/or 1N nitric acid. Heat in water and add 1 ml sodium chromate. Stir for 10 minutes to precipitate barium. Centrifuge, and discard precipitate. Repeat.

10.8 Add 2 ml concentrated ammonium hydroxide to supernate and swirl tube to mix well. Add 2 ml 3N sodium carbonate to reprecipitate strontium. Centrifuge, and discard supernate.

10.9 Wash precipitate with distilled water. Centrifuge, and discard supernate. Repeat.

10.10 Dissolve precipitate in a maximum of 6 ml 6N nitric acid. Add 30 ml 90% nitric acid to solution to precipitate strontium nitrate. Cool solution in an ice bath. Centrifuge, and discard supernate. Record time and date as T_1 (start of yttrium ingrowth).

10.11 Transfer precipitate to a clean, tared planchet with a minimum of distilled water. Dry, cool, and weigh. Count on a low-background beta counter.

10.12 Count again 7 days later for yttrium-90 ingrowth and strontium-89 decay.

10.13 To prepare the resin in the Na^+ form, wash 170 ml of resin (H^+ form) with 1000 ml of 4N sodium chloride eluted at 10 ml/min, followed by 400 ml of 5% sodium hydroxide at 10 ml/min, then 1000 ml distilled water at 10 ml/min flow rate. Pack column and add glass-fiber filter to top of column.

SOUR MILK

10.14 Add 300 ml EDTA complexing solution to 1 liter of milk. Stir, adjust pH to 5.2 with ammonium hydroxide.

10.15 Add 40 ml cation resin to solution and stir for 15 minutes using a magnetic stirrer. Allow resin to settle and decant milk into another beaker containing 40 ml cation resin. Stir again for 15 minutes on a magnetic stirrer. Allow resin to settle and discard the milk.

10.16 Combine the two 40-ml portions of resin and wash several times with distilled water to remove milk and cream. Transfer resin into an 80-ml polyethylene column attached to the top of a 45-ml polyethylene column containing 30 ml cation resin.

10.17 Attach reservoir to top of columns.

10.18 Continue with the procedure for fresh milk beginning with step 10.3.

11. Calibration

Counting efficiency of the low-background beta counter is determined by three factors; geometry, backscatter, and self-absorption. The first two, geometry and backscatter, are fairly well established for each instrument while the third, self-absorption, is dependent on the sample. Therefore, "self-absorption curves" similar to the curves illustrated in Figures 2 and 3, must be prepared. Samples with known activity, but with varying sample weights, are prepared and the data plotted as indicated in Figures 2 and 3. The strontium-89, strontium-90/yttrium-90 standards are traceable to the National Bureau of Standards.

11.1 Reagents

11.1.1 Strontium nitrate stock solution, 20 mg/ml: Dissolve 20 g strontium nitrate in 800 ml distilled water and dilute to 1000 ml.

11.1.2 Strontium-89, ∿1000 pCi/ml: Prepare by diluting a National Bureau of Standards standard with distilled water.

11.1.3 Strontium-90/yttrium-90, ∿1000 pCi/ml: Prepare by diluting a National Bureau of Standards standard with distilled water.

11.1.4 Nitric acid, 90%: Reagent grade.

11.1.5 Nitric acid, 6N: Add 375 ml of concentrated nitric acid to 600 ml of distilled water. Cool and dilute to 1000 ml.

11.1.6 Yttrium carrier, 5 mg/ml: Dissolve 6.15 g yttrium oxide in a minimum of concentrated nitric acid. Dilute to 1000 ml with distilled water.

11.2 Strontium-89 calibration

11.2.1 Weigh 1.0 g strontium-89 solution into each of ten 40-ml centrifuge tubes. Pipet, in increasing quantities, 1 to 10 ml of the strontium nitrate stock solution into these tubes. Mix well.

11.2.2 Transfer to a tared planchet. Rinse centrifuge tubes twice with distilled water and evaporate to dryness.

11.2.3 Dry planchet at 105^{o} C. Cool and reweigh.

11.2.4 Count planchet in low-background beta counter for 50 minutes.

11.2.5 Plot data on graph paper. Recount, or replace any sample that appears to be more than 2 sigma out of line.

11.3 Strontium-90, yttrium-90 calibration

Counting efficiencies must be determined for strontium-90, yttrium-90, and the mixture of strontium-90 and yttrium-90.

11.3.1 Weigh 1.0 g of strontium-90/yttrium-90 standard into each of ten 40-ml centrifuge tubes. Pipet, in increasing quantities, 1 to 10 ml of strontium nitrate stock solution. Bring all volumes to 15 ml with distilled water.

11.3.2 Add 2 ml 6N sodium hydroxide and 10 ml 3N sodium carbonate. Heat with stirring for 5 minutes. Cool and centrifuge. Discard supernate. Record the time as T_1. Hold for 2 weeks or longer to allow the ingrowth of yttrium-90.

11.3.3 At the end of the yttrium-90 ingrowth, dissolve the strontium carbonate with a minimum of 6 ml 6N nitric acid; add 1 ml yttrium carrier (5 mg/ml). Add 30 ml 90% nitric acid to precipitate the strontium nitrate. Cool in an ice bath for 30 minutes and centrifuge. Transfer the supernate (yttrium-90) to a tared planchet and start to evaporate the acid.

11.3.4 Redissolve the strontium nitrate in a minimum of 6N nitric acid. Add 30 ml 90% nitric acid. Cool in an ice bath, and centrifuge. Transfer the supernatant liquid to the planchet in 11.3.3 and continue evaporation. When the planchet is dry, flame to remove any excess nitric acid. Cool and reweigh. Count in a low-background beta counter for 50 minutes.

11.3.5 Redissolve the strontium nitrate from 11.3.4 in a minimum of water and transfer to a tared planchet. Evaporate to dryness, flame, cool, and reweigh. Count in a low-background beta counter for 50 minutes.

11.3.6 After the first count of the strontium-90 planchet, continue additional counting daily for 2 weeks. Then count on every second day for 2 additional weeks. Plot strontium-90/yttrium-90 counts per minute versus strontium-90 counts per minute. This will generate a series of curves based on sample weights.

11.3.7 Plot data obtained in 11.3.4 and 11.3.5 on graph paper. Recount, or replace any sample that appears to be more than 2 sigma out of line. Figure 9 illustrates typical curves.

12. Quality Control

Reference standards and backgrounds are counted with each set of samples and the counts plotted on control charts. Counts which fall outside the warning and control limits are evaluated for appropriate remedial action.

Standard samples are received from the EMSL-LV Quality Assurance Branch. These samples are analyzed and the results are evaluated by the Quality Assurance Branch and the evaluation returned to the analyst. If the results are unsatisfactory, the reason for the problem is found and all results during the questionable time period are evaluated for possible remedial action.

Approximately 10% of all samples are recycled as blind duplicates. The results of the duplicates are subjected to standard statistical tests and listed in a computer printout both as individual results and as a tabular summary. Results outside control limits are examined for possible remedial action.

13. Calculations

13.1 Strontium-90

$$\text{strontium-90 (pCi/liter)} = \frac{AB - CD}{(1 + EF)A - (1 + GH)C} \times \frac{1}{2.22IJKL}$$

where
- A = decay of strontium-89 from the time of collection to the time of first count
- B = net counts per minute of total strontium on second count
- C = decay of strontium-89 from the time of collection to the time of second count
- D = net counts per minute of total strontium on first count
- E = ratio of the counting efficiencies (yttrium-90/ strontium-90) on the second count
- F = yttrium-90 ingrowth from the time of separation to the time of the second count
- G = ratio of the counting efficiencies (yttrium-90/ strontium-90) on the first count
- H = ingrowth of yttrium-90 from time of separation to time of first count
- I = fractional counting efficiency of strontium-90
- J = fractional chemical yield of strontium
- K = adsorption factor for strontium-90
- L = sample volume (liters)

13.2 Strontium-89

$$\text{strontium-89 (pCi/liter)} = \frac{A - (1 + BC)D}{E} \times \frac{1}{2.22FGHI}$$

where
- A = net counts per minute of total strontium on the first count
- B = yttrium-90 ingrowth from separation to first count
- C = ratio of the counting efficiencies (yttrium-90/ strontium-90) on the first count
- D = net counts per minute of strontium-90 (determined by calculation)
- E = decay of strontium-89 from time of collection to time of first count
- F = adsorption factor for strontium-89
- G = fractional chemical yield of strontium
- H = sample volume (liters)
- I = fractional counting efficiency of strontium-90

14. References

Velton, R. J., Resolution of Strontium-89 and Strontium-90 in Environmental Media by an Instrument Technique. Nuclear Instrumental Methods 42:169. (1966).

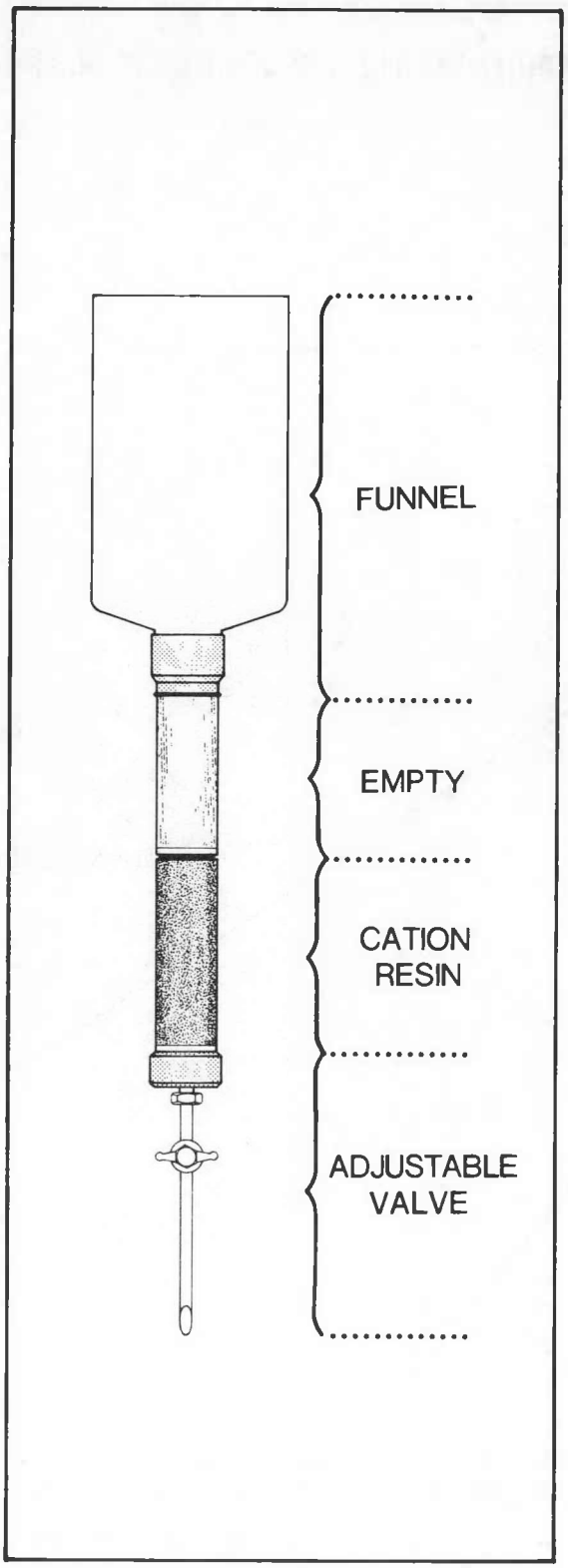

Figure 8. Ion Exchange Column, Strontium Elution.

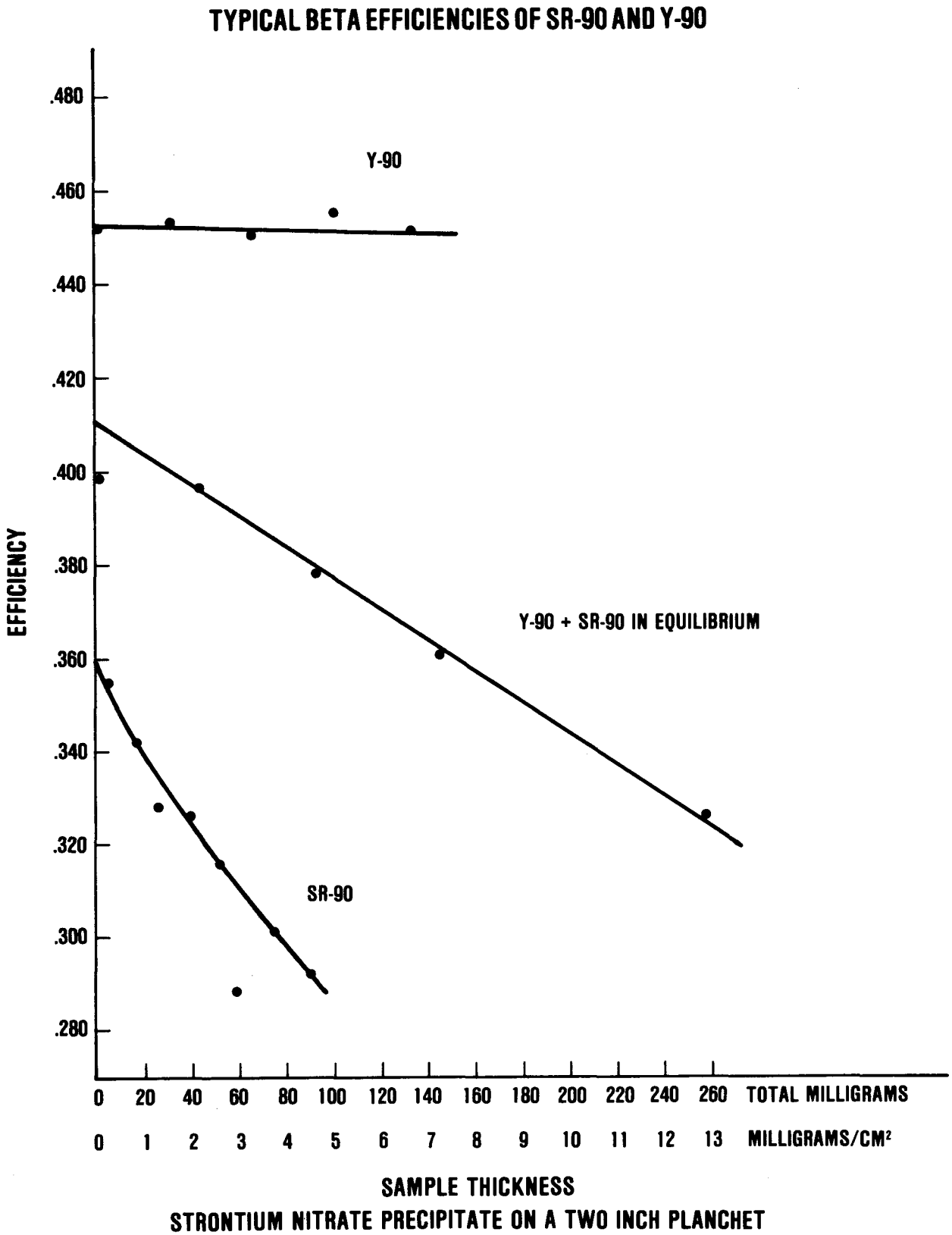

Figure 9. Typical Efficiency Curves.

DETERMINATION OF STRONTIUM-89 AND STRONTIUM-90 IN WATER, VEGETATION, SOIL, AND BIOLOGICAL TISSUE

1. Principle

1.1 Vegetation and animal tissue samples are dry ashed at 600° C to remove all organic material. The ash is dissolved in hydrochloric acid and the appropriate carrier is added. After the addition of disodium ethylenediaminetetraacetate, the sample is passed through a chromatographic column to remove the compressed calcium. The strontium fraction is retained and subsequently eluted with hydrochloric acid. After precipitation as a carbonate, it is converted to a nitrate and mounted for counting.

1.2 Disodium ethylenediaminetetraacetate is added to a water sample and the strontium is determined, as described in 1.1. Chemical yield is determined gravimetrically.

1.3 Soil samples are fused with a mixture of sodium hydroxide-sodium carbonate. The fused mass is dissolved in hydrochloric acid, and the strontium is recovered by the ion-exchange method.

2. Application

2.1 This method is applicable for the determination of strontium-89 and strontium-90 in freshwater, seawater, soil, vegetation, and animal tissue.

3. Range

3.1 No range has been established.

4. Interferences

4.1 Magnesium is the most common interference, and must be removed by precipitating the magnesium complex.

4.2 Other radionuclides usually present do not interfere.

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.

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

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

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 (α) = .05.

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

6.1 The expected precision for strontium-89 and strontium-90 based on the 95% confidence level in food, soft tissue, bone, and water is 3.0 pCi/liter or gram up to a concentration of 30 pCi/liter or gram and 10% above 30 pCi/liter. These precision values are those used in the duplicate analysis program and recommended by the EMSL-LV Quality Assurance Branch.

7. Shipment and storage of samples and sample stability

7.1 Water samples must be preserved with 15 ml of concentrated nitric acid per 3.7 liters (one gallon). Soil samples require no preservation and vegetable or animal tissue must be kept refrigerated. With the proper preservation, samples may be stored for several years for strontium-90 analysis. If strontium-89 analysis is required, samples should be analyzed within two months of collection time.

8. Reagents

8.1 Ammonium acetate buffer solution, pH 5.2: Dissolve 153 g ammonium acetate in 800 ml distilled water and add 28.6 ml glacial acetic acid. Adjust to pH 5.2 using either ammonium hydroxide or acetic acid. Dilute to 1000 ml with distilled water.

8.2 Ammonium hydroxide, concentrated: Reagent grade.

8.3 Ammonium hydroxide, 6N: Dilute 400 ml concentrated ammonium hydroxide to 1000 ml with distilled water.

8.4 Barium carrier, 40 mg/ml: Dissolve 76.2 g barium nitrate in 800 ml distilled water and dilute to 1000 ml.

8.5 Calcium carrier, 2M: Dissolve 328.2 g calcium nitrate in 800 ml distilled water, and dilute to 1000 ml.

8.6 Ethylenediaminetetraacetate disodium (EDTA): Reagent grade.

8.7 EDTA, 6%: Dissolve 66.6 g EDTA in 900 ml distilled water, and dilute to 1000 ml.

8.8 Hydrochloric acid, 6N: Add 500 ml concentrated hydrochloric acid to 400 ml distilled water. Cool, and dilute to 1000 ml.

8.9 Nitric acid, concentrated: Reagent grade.

8.10 Nitric acid, 90%: Reagent grade.

8.11 Nitric acid, 1N: Add 62.5 ml concentrated nitric acid to 800 ml distilled water. Cool, and dilute to 1000 ml.

8.12 Sodium carbonate, 3N: Dissolve 159 g sodium carbonate in 800 ml distilled water and dilute to 1000 ml.

8.13 Sodium chloride, 4N: Dissolve 234 g sodium chloride in 800 ml distilled water and dilute to 1000 ml.

8.14 Sodium chloride, 1.5N: Dissolve 88 g sodium chloride in 800 ml distilled water and dilute to 1000 ml.

8.15 Sodium chromate, 1N: Dissolve 81 g sodium chromate in 800 ml distilled water and dilute to 1000 ml.

8.16 Sodium hydroxide, 6N: Dissolve 240 g sodium hydroxide in 800 ml water. Cool, and dilute to 1000 ml.

8.17 Strontium carrier, 40 mg/ml: Dissolve 96.6 g strontium nitrate in 800 ml distilled water and dilute to 1000 ml.

9. Apparatus

9.1 Parr acid digestion bomb.

9.2 Low-background beta counter.

9.3 Furnace, muffle.

10. Procedure

FOOD, VEGETATION, OR ANIMAL TISSUE

10.1 Dry ash all samples at 600° C to remove all organic matter. Do not exceed 600° C.

10.2 Weigh amount of sample and add carrier as indicated in the following table, into a 250-ml beaker. Add 20 ml 6N hydrochloric acid and with gentle heat dissolve the residue. Add 100 ml distilled water. If insoluble residue (silica) is present, filter, wash residue twice with 100-ml portions of distilled water, and add to filtered solution. Discard residue.

Various Sample Types, Sample Sizes, and Carriers

Sample Type	Sample Size (g)	Strontium carrier (ml)	Calcium carrier (ml)	Barium carrier (ml)
Food	10	2	--	5
Bone	2	2	--	5
Vegetation	2 or 5	2	1	5
Tissue	2	2	1	5

10.3 Add filtrate to 500 ml 6% EDTA solution and adjust to pH 3.8 with concentrated ammonium hydroxide. Stir vigorously for 75 minutes to precipitate the magnesium salt of EDTA. Allow precipitate to settle overnight.

10.4 Filter, and collect the filtrate. Adjust to pH 4.6 with ammonium hydroxide. Add 20 ml sodium acetate buffer solution. Readjust pH to 4.6 with either ammonium hydroxide or acetic acid.

10.5 Quantitatively transfer to the 1000-ml graduated cylinder, dilute to 1000 ml with distilled water. Mix.

10.6 Prepare ion-exchange resin by passing 1000 ml 4N sodium chloride over 170 g of the resin in a column at a flow of 10 ml/min. Follow with 400 ml 5% sodium hydroxide and then with 1000 ml distilled water at a flow of 10 ml/min.

10.7 Assemble apparatus as illustrated in Figure 10. Adjust solution flow through resin column to 10 ml/min. Stop flow when just enough solution remains to cover resin. Discard effluent.

10.8 Transfer 600 ml 2% EDTA, adjusted to pH 5.1 with ammonium hydroxide, to the reservoir and adjust flow to 20 ml/min. Wash column with 200 ml distilled water at a flow of 20 ml/min. Discard washing.

10.9 Place 460 ml 1.5N hydrochloric acid in reservoir, and elute at a flow rate of 8 ml/min. Discard first 60 ml of effluent. Collect the strontium fraction in the next 400 ml in an 800-ml beaker.

10.10 Add 200 ml concentrated ammonium hydroxide to the strontium fraction. Slowly add 10 ml 3N sodium carbonate, and stir for 30 minutes.

10.11 Filter through Millipore filter #URWPO-2400. Rinse the beaker with distilled water. Police sides and bottom of beaker. Wash walls of beaker and filter with ethyl alcohol.

10.12 Wash precipitate from filter into a 40-ml centrifuge tube using a minimum of distilled water. Dissolve precipitate with a maximum of 6 ml 6N nitric acid. Add 30 ml 90% nitric acid to precipitate the strontium

nitrate. Cool solution in ice bath. Centrifuge, and discard supernate. Record data and time as T_1 (start of yttrium ingrowth).

10.13 Transfer precipitate to a clean, tared planchet with a minimum of distilled water. Dry, cool, and weigh. Count on a low-background beta counter.

10.14 Count again seven days later for yttrium-90 ingrowth and strontium-89 decay.

FRESHWATER

10.15 Add 33.3 g EDTA, 2 ml strontium carrier, 1 ml each barium and calcium carrier, to 100-ml water sample. Adjust pH to 4.6 with ammonium hydroxide and proceed as in step 10.4.

SEAWATER

10.16 Add 2 ml strontium carrier and 1 ml each of barium and calcium carrier to 1000 ml of the sample. Stir and heat to boiling.

10.17 Adjust pH to 10.0 with sodium hydroxide. Add 20 ml 3N sodium carbonate. Stir and continue heating until precipitate forms. Cool overnight and decant supernate.

10.18 Dissolve precipitate with 200 ml 6N hydrochloric acid. Adjust volume to 1000 ml with distilled water, and filter. Discard filter. Add 33.3 g EDTA with stirring and adjust pH to 3.8 with ammonium hydroxide. Proceed as in step 10.4.

BONE

10.19 Dissolve 2.0 g of ash in 20 ml 6N hydrochloric acid. When dissolved, add 1000 ml of distilled water, carriers as indicated in table, and proceed as in step 10.4.

11. Calibration

Counting efficiency of the low-background beta counter is determined by three factors; geometry, backscatter, and self-absorption. The first two, geometry and backscatter, are fairly well established for each instrument, while the third, self-absorption, is dependent on the sample. Therefore, "self-absorption curves" similar to the curves illustrated in Figures 2 and 3, must be prepared. Samples with known activity, but with varying sample weights, are prepared and the data plotted as indicated in Figures 2 and 3. The strontium-89, strontium-90/yttrium-90 standards are traceable to the National Bureau of Standards.

11.1 Reagents

11.1.1 Strontium nitrate stock solution, 20 mg/ml: Dissolve 20 g strontium nitrate in 800 ml distilled water and dilute to 1000 ml.

11.1.2 Strontium-89, ∿1000 pCi/ml: Prepare by diluting a National Bureau of Standards standard with distilled water.

11.1.3 Strontium-90/yttrium-90, ∿1000 pCi/ml: Prepare by diluting a National Bureau of Standards standard with distilled water.

11.1.4 Nitric acid, 90%: Reagent grade.

11.1.5 Nitric acid, 6N: Add 375 ml of concentrated nitric acid to 600 ml of distilled water. Cool and dilute to 1000 ml.

11.1.6 Yttrium carrier, 5 mg/ml: Dissolve 6.15 g yttrium oxalate in a minimum of concentrated nitric acid. Dilute to 1000 ml with distilled water.

11.2 Strontium-89 calibration

11.2.1 Weigh 1.0 g strontium-89 solution into each of ten 40-ml centrifuge tubes. Pipet, in increasing quantities, 1 to 10 ml of the strontium nitrate stock solution into these tubes. Mix well.

11.2.2 Transfer to a tared planchet. Rinse centrifuge tubes twice with distilled water and evaporate to dryness.

11.2.3 Dry planchet at 105° C. Cool and reweigh.

11.2.4 Count planchet in low-background beta counter for 50 minutes.

11.2.5 Plot data on graph paper. Recount, or replace, any sample that appears to be more than 2 sigma out of line.

11.3 Strontium-90, yttrium-90 calibration

Counting efficiencies must be determined for strontium-90, yttrium-90, and the mixture of strontium-90 and yttrium-90.

11.3.1 Weigh 1.0 g of strontium-90/yttrium-90 standard into ten 40-ml centrifuge tubes. Pipet in increasing quantities, 1 to 10 ml of strontium nitrate stock solution, bringing all volumes to 15 ml with distilled water.

11.3.2 Add 2 ml 6N sodium hydroxide and 10 ml 3N sodium carbonate. Heat with stirring for five minutes. Cool and centrifuge. Discard supernate. Record the time as T_1. Hold for two weeks or longer to allow the ingrowth of yttrium-90.

11.3.3 At the end of the yttrium-90 ingrowth period, dissolve the strontium carbonate with a minimum of 6 ml 6N nitric acid; add 1 ml yttrium carrier (5 mg/ml). Add 30 ml 90% nitric acid to precipitate the strontium nitrate. Cool in an ice bath for 30 minutes; centrifuge. Transfer the supernate, containing the yttrium, to a tared planchet and start to evaporate the acid.

11.3.4 Redissolve the strontium nitrate in a minimum of 6N nitric acid. Add 30 ml 90% nitric acid. Cool in an ice bath, and centrifuge. Transfer the supernatant liquid to the planchet in 11.3.3 and continue evaporation. When the planchets are dry, flame to remove any excess nitric acid. Cool and reweigh. Count in a low-background beta counter for 50 minutes.

11.3.6 After counting the strontium-90 planchet, continue counting daily for two weeks. Then count on every second day for two weeks. Plot strontium-90/yttrium-90 counts per minute versus strontium-90 counts per minute. This will generate a series of curves based on sample weights.

11.3.7 Plot data obtained in 11.3.4 and 11.3.5 on graph paper. Recount, or replace, any sample that appears to be more than two sigma out of line.

12. Quality Control

Reference standards and backgrounds are counted periodically and counts plotted on control charts. Counts which fall outside the warning and control limits are evaluated for appropriate remedial action.

Standard samples are received from the EMSL-LV Quality Assurance Branch. These samples are analyzed and the results are evaluated by the Quality Assurance Branch and evaluation returned to analyst. If the results are unsatisfactory, the reason for the problem is found and all results during the questionable time period are evaluated for possible remedial action.

Approximately 10% of all samples are recycled as blind duplicates. The results of the duplicates are subjected to standard statistical tests and listed in a computer printout both as individual results and as a tabular summary. Results outside control limits are examined for possible remedial action.

13. Calculations

13.1 Strontium-90

$$\text{strontium-90 (pCi/g or liter)} = \frac{AB - CD}{(1 + EF)A - (1 + GH)C} \times \frac{1}{2.22IJKL}$$

where
- A = decay of strontium-89 from the time of collection to the time of first count
- B = net counts per minute of total strontium on second count
- C = decay of strontium-89 from the time of collection to the time of second count
- D = net counts per minute of total strontium on first count
- E = ratio of the counting efficiencies (yttrium-90/strontium-90) on the second count
- F = yttrium-90 ingrowth from the time of separation to the time of the second count
- G = ratio of the counting efficiencies (yttrium-90/strontium-90) on the first count

H = ingrowth of yttrium-90 from time of separation to time of first count

2.22 = dpm/pCi

I = fractional counting efficiency of strontium-90

J = fractional chemical yield of strontium

K = adsorption factor for strontium-90

L = sample (grams or liters)

13.2 Strontium-89

$$\text{strontium-89 (pCi/g or liter)} = \frac{A - (1 + BC)D}{E} \times \frac{1}{2.22FGHI}$$

where A = net counts per minute of total strontium on the first count

B = yttrium-90 ingrowth from separation to first count

C = ratio of the counting efficiencies (yttrium-90/strontium-90) on the first count

D = net counts per minute of strontium-90 (determined by calculation)

E = decay of strontium-89 from time of collection to time of first count

2.22 = dpm/pCi

F = adsorption factor for strontium-89

G = fractional chemical yield of strontium

H = sample size (grams or liters)

14. References

Velton, R. J., Resolution of Strontium-89 and Strontium-90 in Environmental Media by an Instrument Technique. Nuclear Instrumental Methods 42:169. (1966).

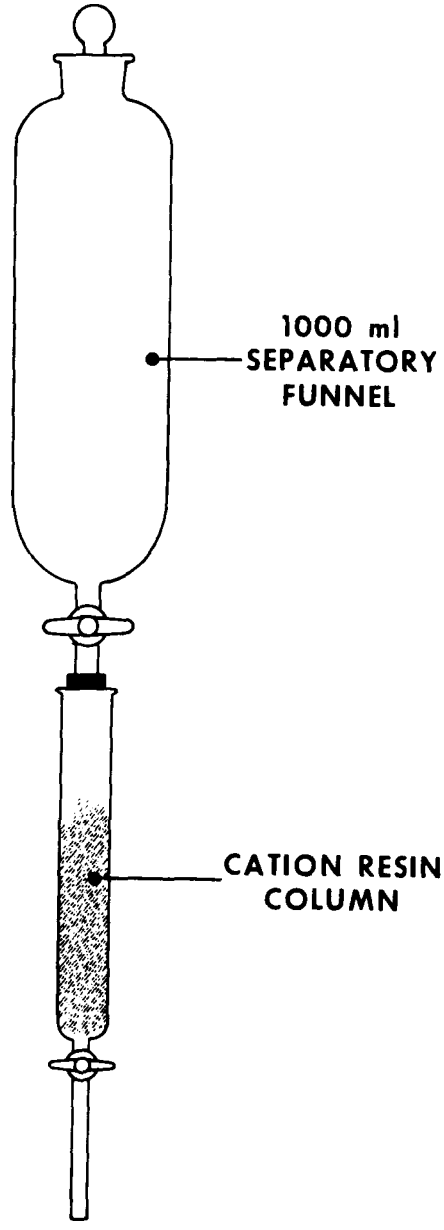

Figure 10. Ion-Exchange Apparatus.

THE COLLECTION AND DETERMINATION OF TRITIUM IN AIR

1. Principle

1.1 This method describes a procedure for the collection and determination of tritium as hydrogen and as moisture in the atmosphere. The atmospheric sample is passed through a molecular sieve to remove the water vapor. Tritium-free hydrogen is added as a carrier. The carrier, hydrogen and atmospheric hydrogen, are converted to water using a palladium black catalyst. This water is collected in a second molecular sieve trap. The water collected on these traps is removed by heating and is subsequently analyzed for tritium.

2. Application

2.1 This method is applicable for the collection and determination of tritium in air. A one-week sample is usually collected.

3. Range

3.1 No range has been determined.

4. Interferences

4.1 Gaseous radionuclides that might be collected on the molecular sieve and subsequently removed are the only interferences.

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.

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

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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

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

E = fractional counting efficiency
S = sample size

6. Precision and accuracy

6.1 The estimated precision at the 1 pCi/m^3 level is ± 10 percent.

7. Shipment and storage of samples and sample stability

7.1 Samples are collected on a weekly basis and returned to the laboratory. Analysis should be performed within 48 hours.

8. Reagents

8.1 Electrolyte, 2% sodium hydroxide: Dissolve 20 g sodium hydroxide pellets in 800 ml low-level-tritium distilled water and dilute to 1000 ml.

8.2 Liquid scintillation cocktail: Prepare by dissolving 8.0 g 2.5-diphenyloxazole (PPO), 1.5 g p-bis-(O-methylstyrl) - benzene (BIS-MSB), and 120 g naphthalene in 800 ml spectrographic grade p-dioxane and dilute to 1000 ml. Store in amber bottle. The solution is not usable after one month.

8.3 Molecular sieve-4A, 1/8" x 3/16" pellets:

8.4 Palladium black catalyst: Prepare by slurring 250 g of filter-grade asbestos in 1000 ml low-level-tritium distilled water. Add 10 g palladium chloride dissolved in 25 ml concentrated hydrochloric acid. Stir for 5 minutes and add 50 ml concentrated ammonium hydroxide and 100 ml 37% formaldehyde (solution should be black). Continue stirring for 10 minutes. Filter and wash with low-level-tritium distilled water. Dry at 350° C before using.

9. Apparatus

The total sampler consists of two parts: a "field box," and a permanently located field station.

"FIELD BOX"

9.1 A foam-filled box with cutouts for the traps.

9.2 M1 and M2 trap: 250 g molecular sieve-4A heated to 350° C and evacuated at 1 mm of mercury pressure.

9.3 MH trap, 75 mm x 25 mm: 400 g molecular sieve-4A heated to 350° C and evacuated at 1 mm of mercury pressure.

9.4 Hydrogen generator: Consists of a 200-ml plastic bottle with two platinum electrodes.

"FIELD STATION"

9.5 Refrigerator: approximately 2.5 cu ft

9.6 Rectifier: 1 amp capacity

9.7 Pump: fish tank

9.8 Flowmeter: 0 to 10 ml/min

9.9 Meter: dry gas

LABORATORY

9.10 Furnace: 350° C

9.11 Trap, Johns

9.12 Tube, connecting

9.13 Dewar, 1000-ml

9.14 Pump, vacuum, 130 l/min

9.15 Bottle, weighing

9.16 Pipet, disposable, 5 ml

9.17 Vial, polypropylene, 25 ml

10. Procedure

10.1 Label glass traps with station number and position, i.e., M1, M2, MH. Record weight and other data on worksheet.

10.2 Fill the electrolytic cell with 70 ml electrolyte, weigh, and record.

10.3 Place traps and electrolytic cell in the "field box" and make connection as illustrated in Figure 11.

SAMPLER PREPARATION IN THE FIELD

10.4 Connect "field box" to system, Figure 12.

10.5 Turn on pump and check for leaks. This is accomplished by pinching intake hose and observing the float in the flowmeter. Float should return to zero. All leaks must be corrected before proceeding.

10.6 Remove clamp from electrolytic cell.

10.7 Install a new chart in the recording thermometer.

10.8 Record gas meter reading, air flow-rate, date and hour, sampler number, and station sample card.

SAMPLE REMOVAL

10.9 Check for leaks as before and note on worksheet if any were observed.

10.10 Record flow, gas meter reading, date and time on the sample card. Remove temperature chart. Return it with the sampler and sample card.

LABORATORY DISASSEMBLY

10.11 Remove and weigh the electrolytic cell and glass traps. Record on worksheet.

WATER RECOVERY

10.12 Place M1 or MH trap in distillation unit. Adjust heat to obtain 350° C in 30 minutes. Distill the water into the trap cooled in liquid nitrogen. Use helium as a carrier. All of the water should distill in one hour. If weight of water on M1 or MH is less than 9 g, add appropriate volume of distilled low-level-tritium well water to make 10 ml before distillation.

10.13 Turn off the helium carrier gas and vacuum; remove the trap from liquid nitrogen. Allow trap to come to room temperature. Record weight of water recovered on worksheet.

10.14 Pipet 5 ml of water into a liquid scintillation vial and add 20 ml liquid scintillation solution. Prepare a background and standard vial. Place in liquid scintillation spectrometer and allow to dark-adapt for 24 to 36 hours before counting.

10.15 De-gas M2 as in steps 10.11 and 10.12 for reuse. Do not save this water.

11. Calibration

12. Quality Control

12.1 A portable sampler is being used to collect a duplicate sample at various sampling stations. This sample is analyzed as a blind duplicate to collect sampling error information.

13. Calculations

13.1 Volume sample at STD $(M^3) = \dfrac{V_1 \times P_1 \times 273}{760 \times (273 + T_1)}$

where V_1 = volume collected (m^3)

P_1 = average barometric pressure

273 = absolute temperature equal to 0° C

760 = mm of mercury at sea level

T_1 = average temperature (from temperature chart)

13.2 Tritium as water (pCi/m^3 air) $= \dfrac{A_{M1} \times V_{M1}}{V_o}$

where A_{M1} = pCi/l of water recovered from M1

V_{M1} = volume of water recovered from M1

V_o = volume of sample from 13.1

13.3 Tritium as hydrogen (pCi/m^3) $= \dfrac{A_{MH} \times V_{MH}}{V_o \times H_E}$

where A_{MH} = pCi/ml of water recovered from MH

V_{MH} = volume of water recovered from MH

V_o = volume of sample from 13.1

$H_E = \dfrac{\text{weight water on MH}}{\text{weight loss from cell - weight water on MH}}$

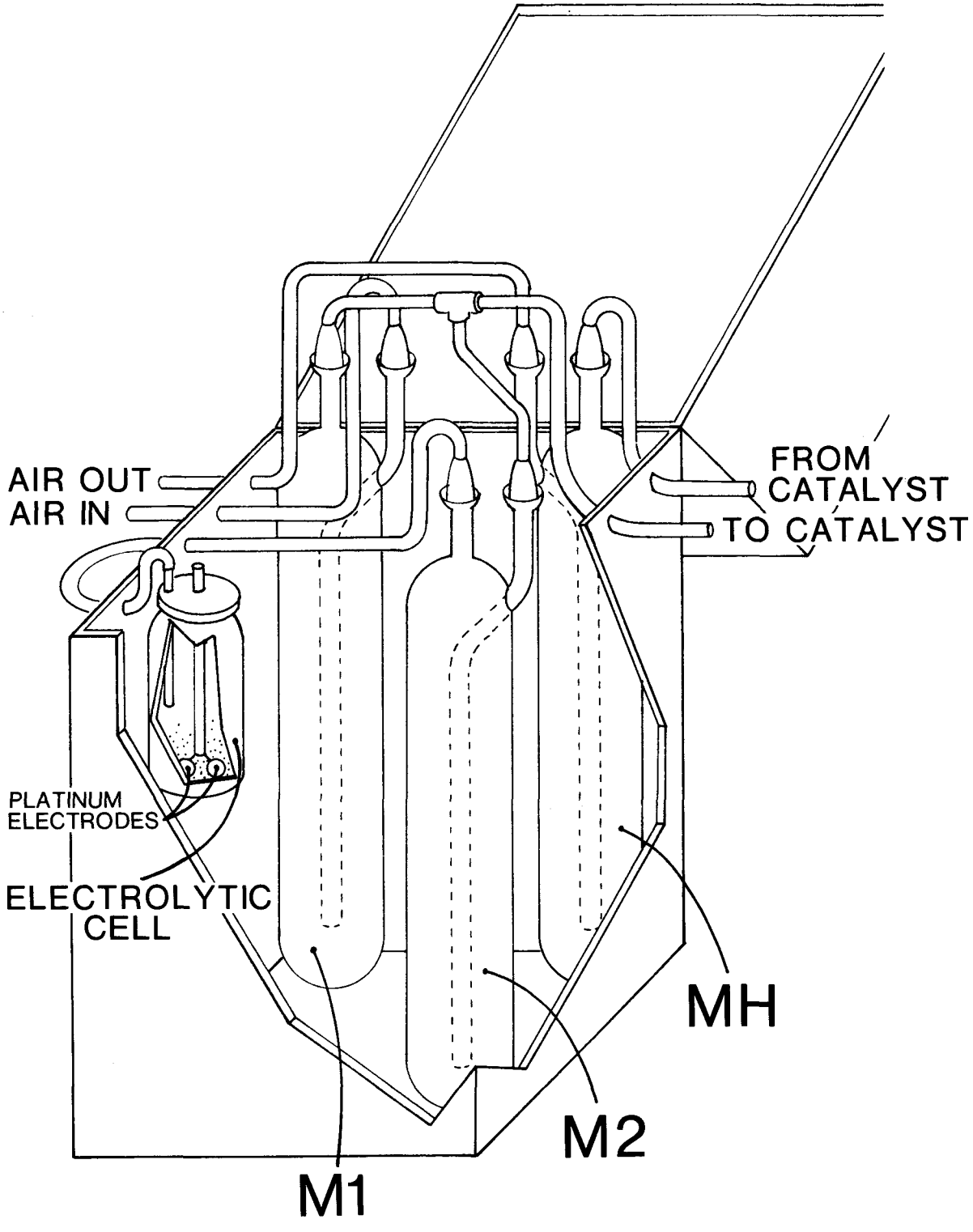

Figure 11. Field Box .

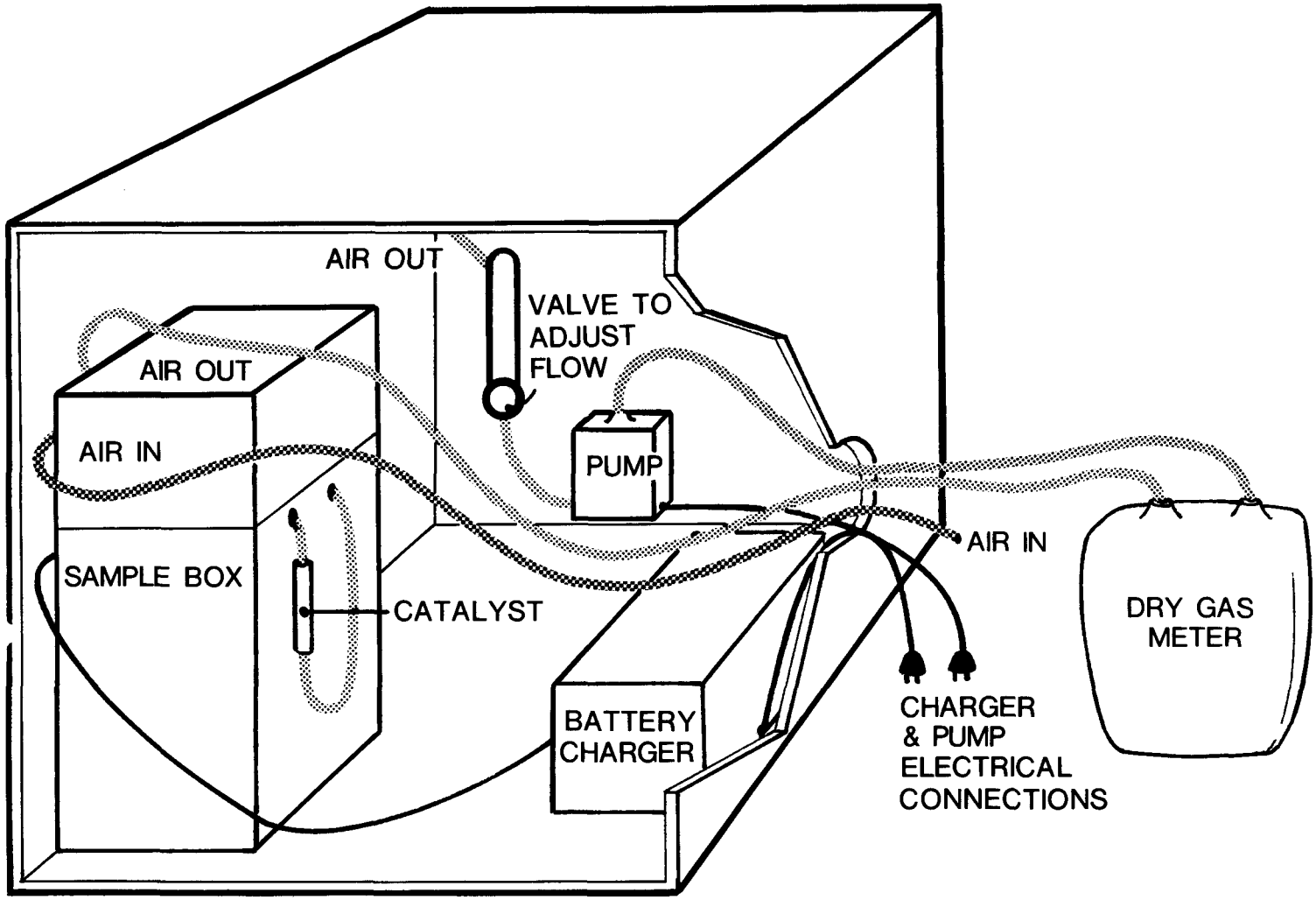

Figure 12. Field Station.

DETERMINATION OF LOW-LEVEL TRITIUM IN WATER
(Alkaline Electrolytic Enrichment)

1. Principle

Distilled water with added sodium hydroxide is slowly electrolyzed at a constant temperature. The protium atom is preferentially evolved leaving the tritium atom behind. The complete theoretical discussion of the separation is presented by Östund, 1962.

2. Application

2.1 The method is applicable for the determination of tritium at low levels for all distilled waters.

3. Range

An upper level of 250 pCi/liter has been established. Cross-contamination becomes a problem at higher ranges.

4. Interferences

4.1 Other radionuclides and stable elements present in water do not interfere.

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.

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

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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

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

6. Precision and accuracy

7. Shipment and storage of sample and stability

7.1 Samples must be collected in glass without preservatives. A minimum of 300 ml are needed for the analysis. Samples may be stored one year in glass.

8. Reagents

8.1 Carbon dioxide, gas, commercial grade

8.2 Potassium permanganate crystal, reagent grade

8.3 Silver nitrate, crystal, reagent grade

8.4 Sodium hydroxide, pellets, reagent grade

9. Apparatus

9.1 Bottle: 500-ml screw cap

9.2 Condenser, Liebig: 300-mm

9.3 Constant current supply: 3 amp and 0.3 amp are required

9.4 Constant temperature bath: maintained at 4^{o} C

9.5 Electrolytic cell: (Figure 13)

9.6 Flask, round bottom: 1000-ml

9.7 Flask, volumetric: 200-ml

9.8 Pipet, disposable: 5-ml

9.9 Pipet, volumetric: 50-ml

9.10 Pump, vacuum:

9.11 Trap, receiving: 50-ml

9.12 Tube, adapter: 105^{o}

9.13 Tube, connecting: 75^{o}

9.14 Tube, connecting: 35/40 to 18/9

10. Procedure

10.1 Transfer 300 to 500 ml of sample to a 1000-ml flask. Any settled solids may be discarded. Add a few crystals of potassium permanganate to form a permanent pink-colored solution. Add one boiling chip.

10.2 Distill to dryness, discarding first few drops. Collect in a glass screw-top bottle.

10.3 Clean the electrolytic cells with distilled water, rinse with ethyl alcohol, and bake dry at 350° C. Cool.

10.4 Pipet 50 ml of the sample into the electrolytic cell. Add 1 g (7 pellets) sodium hydroxide pellets. Dissolve by capping and mixing thoroughly. (A 2% sodium hydroxide solution is required as serious corrosion problems will result.)

10.5 Remove stopper and insert the clean iron-nickel electrode assembly. Add the glass tops with red and black leads extending through the side arm.

10.6 Prepare a low-level standard (20 to 30 TU) and a background (antique water) sample for each group of eight samples. Place all electrolytic cells in constant temperature bath. Fill 200-ml volumetric flasks with a portion of sample, standard, or background.

10.7 Connect all cells in series and connect the iron electrode to the positive lead of the constant current power supply and connect the nickel electrode to the negative lead of the power supply.

10.8 Activate the 3-amp power supply and observe the meter reading. The amp-meter should indicate 3 amperes and the voltmeter should indicate 2.7 volts times the number of cells being used. A lower voltage reading indicates a short circuit and a higher reading indicates an open circuit. Corrective action must be made.

10.9 Cover cells with protective cover as explosions have occurred from this point on.

10.10 When the sample has decreased in volume by 50% (usually 24 hours), readjust volume to 50 ml with an aliquot from the 200-ml volumetric flask. Repeat until all of the 200 ml have been added to the cell.

10.11 Permit the volume to decrease to 25 ml, then decrease the current to 0.3 amp. Continue the electrolysis until the volume decreases to 4 or 5 ml. (If the levels of solution in the cells are not all even, disconnect those that are finished and continue electrolysis.)

10.12 Remove the cells from the constant temperature bath. Replace top and electrode assembly with glass cap.

10.13 Bubble carbon dioxide gas through remaining liquid for 3 to 4 minutes. Replace cap with glass stopper.

10.14 Connect the electrolytic cell to the tared trap with a ground joint adapter. Place a plug of glass wool in the adapter to eliminate entrainment. Connect the assembly to a vacuum pump.

10.15 Immerse trap in liquid nitrogen and apply vacuum. When initial gassing and boiling ceases, apply heat to electrolytic cell. Continue heating until all visible water has been distilled. Discontinue heat but continue to evacuate for 10 to 15 minutes.

10.16 Disconnect the apparatus, capping the trap. Allow the trap to return to room temperature and weigh.

10.17 Transfer the water from the trap to a tared scintillation vial. Weigh and record the weight of water transferred. If needed, add low-tritium water to the vial until it contains 5 ml.

10.18 Add liquid scintillation cocktail to all vials and prepare one counting standard and one background.

10.19 Place in liquid scintillation spectrometer and dark-adapt for 24 to 36 hours before counting.

10.20 Count each sample twice for 100 minutes each time or until the statistics on 2 succeeding counts are within 2 sigma of each other.

11. Calibration

11.1 Prepare an enrichment curve by enriching a set of standard tritium samples using the same procedure as for the unknowns. Allow the final volume of enriched solution to vary so that different points are obtained for the construction of the curve.

12. Quality control

12.1 As the activity of many of the samples is below the minimum detectable concentration, samples with higher activities are recycled as blind duplicates.

13. Calculations

$$\text{Tritium (TU)} = \frac{A - B}{2.22 \times 3.25 \times 0.005 \times \text{Eff} \times D \times E}$$

where A = gross counts per minute
B = background counts per minute
2.22 = dpm/pCi
3.25 = pCi/TU
0.005 = sample volume counted, liters
Eff = fractional counting efficiency
D = sample dilution factor (volume of sample divided by volume counted, if dilution to 5 ml is necessary)
E = enrichment factor (from calibration graph)

14. References

14.1 Östund, H. G., Werney, E. The Electrolytic Enrichment of Tritium and Deuterium for Natural Tritium Measurements. Proceedings of Tritium in the Physical and Biological Sciences. IAEA, Vienna 1962.

14.2 Harley, J. H. HASL Procedure Manual. HASL-300.

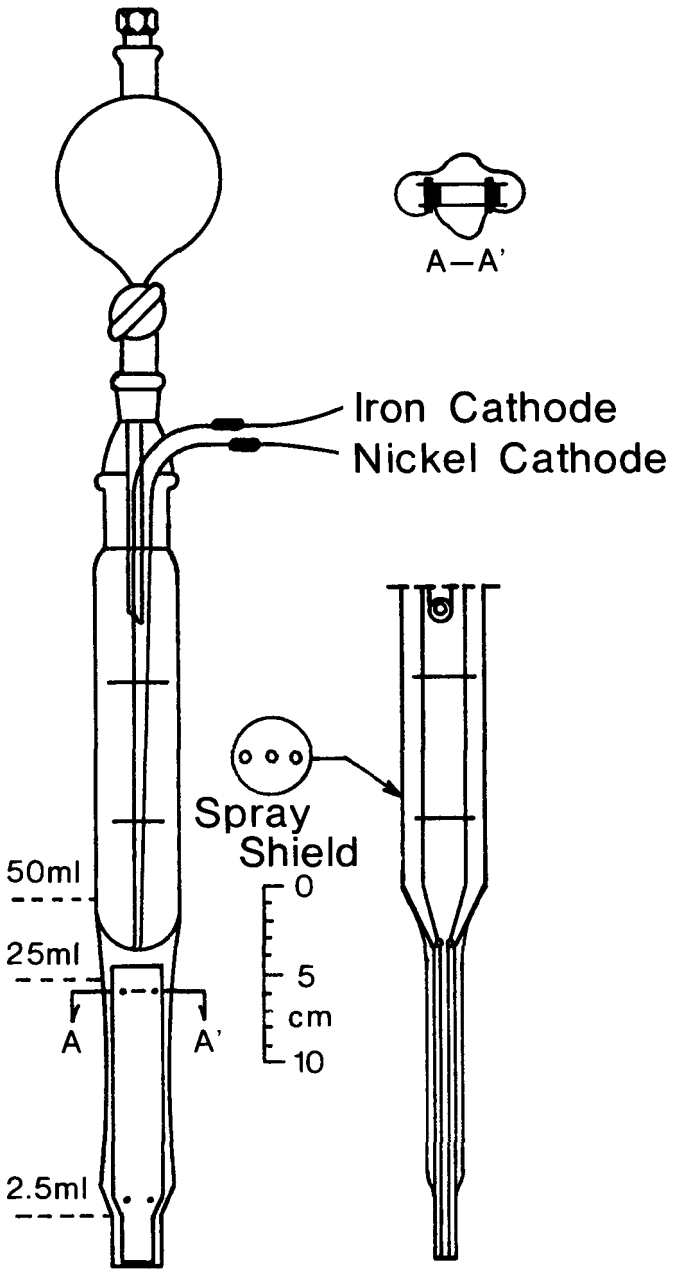

Figure 13. Alkaline Electrolysis Cell.

DETERMINATION OF TRITIUM IN WATER AND BIOLOGICAL TISSUE
(Direct Method)

1. Principle

1.1 A portion of sample is distilled to remove contaminants. Several different techniques are used to recover a pure distilled fraction. These techniques include azeotopic distillation, vacuum distillation, and ambient pressure distillation. Details of these techniques will be discussed under procedure sections. After distillation, an aliquot is mixed with liquid scintillation solution and counted in a liquid scintillation spectrometer. Standards and background samples are prepared and counted with each group of samples.

2. Application

2.1 This method is applicable for the determination of tritium in water, vegetation, animal tissue, blood, and urine.

3. Range

3.1 No range has been established.

4. Interferences

4.1 Volatile radionuclides are the common interference. Alcohols, acids, most OH-radicals and hydrocarbons are common chemical interferences, but all may be eliminated by proper sample preparation.

4.2 Light and chemical phosphorescence must be considered. These can be eliminated by allowing the sample to dark-adapt for 24 to 36 hours.

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.

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

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* 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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

6.1 The expected precision for tritium in water, based on a 95% confidence level analytical error, below 4000 pCi is given by the expression:

$$\%2\sigma = 33970x(pCi/1)^{-0.9067}$$

and 20% above 4000 pCi/1. These are the values used in the Duplicate Analysis Program and are recommended by the EMSL-LV Quality Assurance Branch.

6.2 Over a period of 3 years, 12 cross-check samples containing known amounts of tritium in water, and 12 cross-check samples containing known amounts of tritium in urine were received from the Quality Assurance Branch. None of the results obtained were outside the three-sigma control limits.

7. Shipment and storage of samples

7.1 Water samples should be collected in glass with no preservatives.

7.2 Biological samples should be kept refrigerated until time of analysis.

8. Reagents

8.1 Cyclohexane: Reagent grade.

8.2 Liquid scintillation solution: Prepare by dissolving 8.0 g 2,5-diphenyloxazole (PPO), 1.5 g p-bis-(O-methylstyrl)-benzene (BIS-MSB), and 120 g napthalene in 800 ml spectrographic grade p-dioxane and dilute to 1000 ml. Store in amber bottle. The solution is not usable after one month.

8.3 Silver nitrate, crystals: Reagent grade.

9. Apparatus

9.1 Condensers, Liebig: 100 mm, 300 mm

9.2 Desiccator, vacuum

9.3 Flasks, boiling: 1 neck: 100 ml, 1000 ml

9.4 Trap, Barret

9.5 Trap, Johns

9.6 Tube, connecting: 105^{o}, 75^{o}

Assembled apparatus is illustrated in Figure 14.

10. Procedure

WATER

10.1 Distill 10- to 50-ml portion of sample just to dryness. Vent the first steam and collect the distillate in a cold trap. If radioiodine is present, add 0.1 g silver nitrate before distillation.

10.2 Pipet a 5-ml portion of the distillate into a polyethylene counting vial. Add 20 ml of liquid scintillation solution.

10.3 Prepare a background and standard by pipetting 5 ml of low-tritium water and 5 ml of a diluted National Bureau of Standards standard into polyethylene counting vials. Add 20 ml of liquid scintillation solution to each vial.

10.4 Mix all solutions and place in liquid scintillation spectrometer. Allow to light-adapt for 24 hours or longer. Count for two 100-minute intervals or until successive counts are within 2 sigma.

MILK, BLOOD, AND URINE

10.5 Add 50 ml of sample and 50 ml cyclohexane to boiling flask. Assemble apparatus as illustrated in Figure 14.

10.6 Bring to boiling and collect distillate in Barret trap. Continue distillation until 15 to 20 ml of water are collected. Allow phases to separate and water phase to clear (usually overnight).

10.7 Proceed as in 10.2 for the tritium determination.

VEGETATION OR ANIMAL TISSUE

10.8 Add 100 to 200 g of vegetable material or 25 to 50 g of animal tissue to a vacuum desiccator. Cool trap with liquid nitrogen and apply vacuum.

10.9 Allow the vacuum distillation to continue for several hours until 15 to 20 ml of water are collected.

10.10 Proceed as in 10.1.

11. Calibration

11.1 The prime consideration in calibration of a liquid scintillation spectrometer after an initial determination of operating conditions is to maximize the counting efficiency with the lowest background. The so-called "Figure of Merit" is accomplished by adjusting upper and lower discrimination and gain control as necessary (see Manufacturer's Operator's Manual).

12. Quality Control

12.1 A background and standard are counted along with each group of 10 samples. The data recorded daily on a control chart provide an indication of instrument performance.

13. Calculation

WATER, URINE, MILK, AND BLOOD

13.1 $$\text{Tritium (pCi/liter)} = \frac{1000\ A-B}{2.22\ CD}$$

where
A = gross counts per minute
B = background counts per minute
2.22 = dpm/pCi
C = fractional counting efficiency determined with the standard counted with each group
D = sample size (usually 5 ml)

VEGETATION OR ANIMAL TISSUE

13.2 $$\text{Tritium (pCi/g)} = E \times \text{Tritium (pCi/ml)}$$

where E = fractional water composition (ml/g)

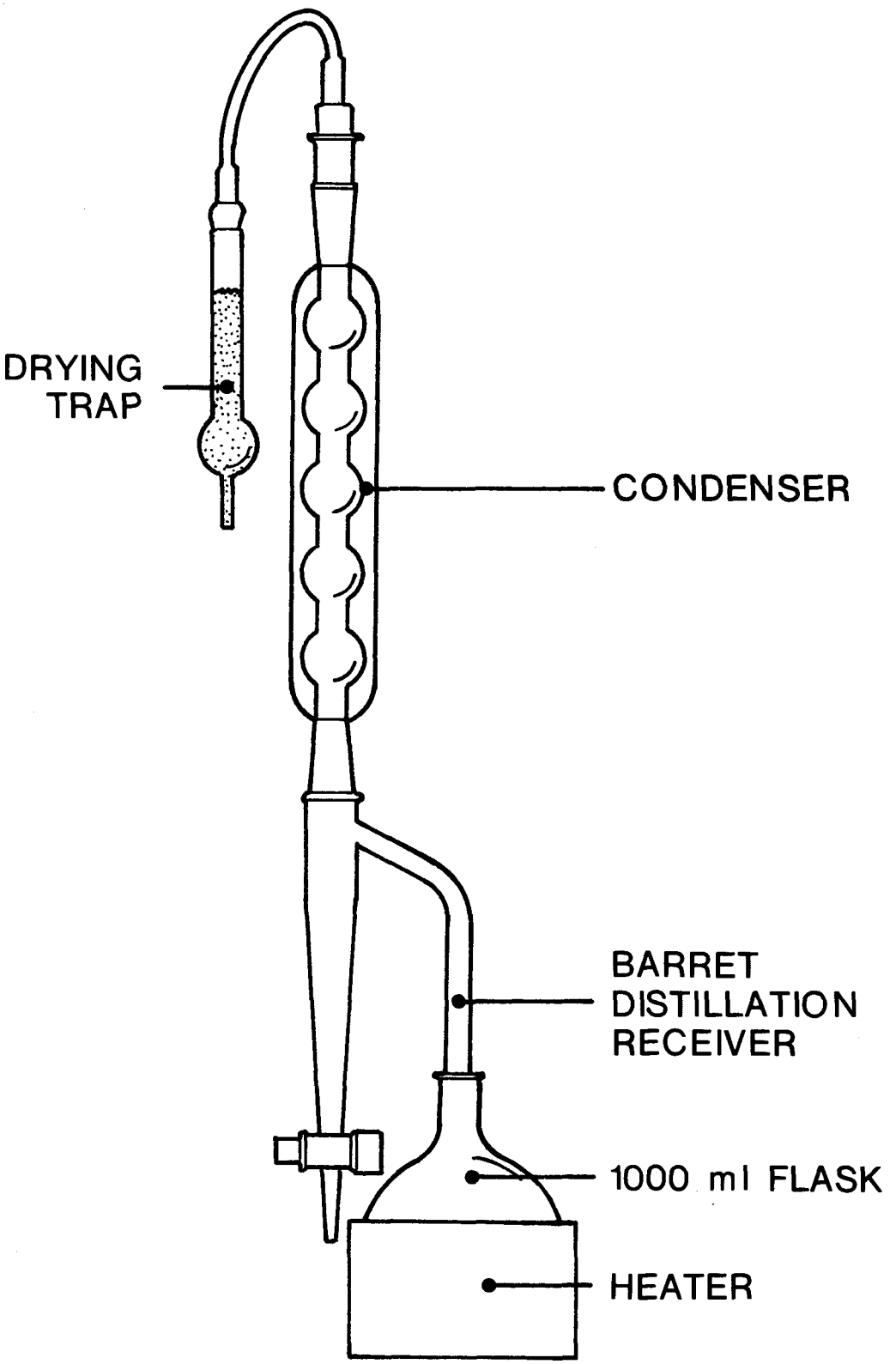

Figure 14. Distillation Apparatus.

ISOTOPIC ANALYSIS BY GAMMA RAY SPECTRA USING LITHIUM-DRIFTED GERMANIUM DETECTORS

1. Principle

1.1 Environmental levels of gamma-emitting radionuclides in a multitude of natural matrices are identified and quantitated by gamma scintillation spectroscopy. However, in numerous cases the success in resolving complex spectra is limited by reason of resolution. In cases where peak multiplets are within the resolution limits of the scintillation detector, computer deconvolution becomes impossible. These cases require the employment of a solid state "high resolution" detector generally constructed of lithium-drifted germanium, Ge(Li). The average resolution advantage of a high-volume Ge(Li) detector over a NaI(Tl) scintillation detector is about 40. For this reason, Ge(Li) detectors are used for the analysis of gamma-emitting radionuclides in the environment.

2. Application

2.1 This method is applicable for analysis of gamma-emitting radionuclides with gamma energies ranging from nearly 60,000 electron volts (60 keV) to approximately 2,000,000 electron volts (2 meV).

3. Range

3.1 There is no upper range for Ge(Li) gamma spectroscopy. The electronics have an upper limit of approximately 3×10^6 detector counts per minute (cpm). If a sample contains radionuclide concentrations resulting in a count rate greater than 3×10^6 cpm, then either the distance between the sample and detector is increased or an aliquot of the sample is analyzed.

4. Interferences

4.1 The use of Ge(Li) detectors has greatly reduced the problem of interferences between gamma photons of nearly identical energies. Spectral peaks containing multiple energy contributions may be deconvoluted when actual photon energies are within 1 keV.

5. Minimum detectable concentrations

5.1 The minimum detectable concentrations (MDC's) of radionuclides vary according to the particular branching ratio of a radionuclide upon disintegration, the counting geometry, the photon energy, sample size, and the actual counting time of detection. One-thousand-minute counts are reasonable for low-level environmental samples. The MDC of cesium-137 for such a count time is approximately 5 picocuries per total sample. This is based on a 200-ml sample placed directly upon the detector.

6. Precision

6.1 The 95% confidence interval for a result obtained by gamma spectroscopy is approximately ± the MDC for samples with gamma activities close to background and ± 10% for samples with "higher" activities, i.e., the 95% interval is ± the MDC or ± 10%, whichever is greater. This is based on nonoverlapping gamma photopeaks. In the case of photopeak multiplets, the precision decreases nonlinearly with the degree of peak overlap.

7. Shipment and storage of samples

7.1 Samples containing or suspected of containing short-lived isotopes require expeditious handling. Care should be exercised with all samples to assure that they are, and remain, representative and homogeneous. This may require the addition of acid to water samples to prevent dissolved radionuclides from plating out on the sample container walls, or the addition of formaldehyde to aid in the preservation of milk samples, etc.

8. Reagents

8.1 Radon-free water is used for dilution of aqueous samples to a constant volume.

9. Apparatus

9.1 Either a 4096- or a 2048-channel multichannel analyzer spectrometer with output compatible to standard computer readable media.

9.2 Large-volume Ge(Li) detector.

10. Procedure

10.1 Prepare homogeneous sample in a standard geometry for counting. This geometry must be equivalent to one for which the detector has been calibrated to generate an appropriate efficiency vs. energy curve.

10.2 Place sample in counting configuration.

10.3 Refer to manufacturer's operating manual for data acquisition and computer operation.

10.4 Print spectrum and/or store on appropriate computer-compatible device.

11. Calibration

11.1 To energy-calibrate, cadmium-109 with a gamma emission at 88 keV and yttrium-88 with a gamma emission at 1836 keV are used. By juggling the amplifier's "gain" and the analog-to-digital converter's "zero offset", the centroids of these peaks are placed in the appropriate locations for a linear "energy-versus-channel-number" calibration. For the 0.5-keV-per-channel calibration, the 88-keV peak centroid is placed at channel 176 and the 1836-keV peak centroid at channel 3672. Due to the high resolution and stability of current Ge(Li) detectors, there should be negligible differential nonlinearity.

11.2 Efficiency calibration is achieved by counting a standard in a given geometry where the concentrations of the isotopes are known. The result of this calibration is an efficiency-versus-energy curve in units of counts per gamma. A mixed-radionuclide source is generally used which produces peaks well spaced and distributed throughout the normal analysis range.

12. Quality Control

12.1 The Ge(Li) system is energy-calibrated daily and efficiency-calibrated as needed. Logs of pertinent calibration data are maintained.

12.2 Approximately 10% of all samples submitted for gamma spectrum analysis are resubmitted as blind samples. The results of these duplicate analyses are subjected to standard statistical tests. A summary of the results from the statistical tests, along with the individual analytical results, is listed in a computer printout. Results outside control limits are examined for possible remedial action.

12.3 Standard samples are received from the EMSL-LV, Quality Assurance Branch, International Atomic Energy Agency in Austria, and the World Health Organization in France. These samples are analyzed and the results are analyzed by the originating office. If the results are unsatisfactory, the reason for the anomaly is found and all results generated during the questionable time period are evaluated for possible corrective action.

13. Calculations

13.1 Isotopic identifications from Ge(Li) gamma spectral data are made as follows:

a. Identify all peak energies.

b. Calculate all peak areas by integrating the peak region and subtracting the area beneath the continuum.

c. Identify isotopes by the presence or absence of appropriate photopeaks and their ratios to each other.

13.2 The concentration calculation for each isotope is:

$$\text{Isotopic Concentration } \left(\frac{\text{picocuries}}{\text{unit of size}}\right) = \frac{A}{2.22 \times B \times E \times S \times T} \quad (1)$$

where
- A = peak area above continuum (counts)
- B = branching ratio for the gamma ray of the particular isotope in question (gammas/disintegration)
- E = fractional detector efficiency at photopeak energy (counts/gamma)
- S = sample size
- T = count length (minutes)

13.3 The 2-sigma counting error is calculated by:

$$\text{Error (\%)} = \frac{2\sqrt{A + 2C}}{A} \times 100$$

where C = photopeak area below continuum (counts)

13.4 The above three paragraphs, 13.1, 13.2, and 13.3, yield results at the time of count. To extrapolate to the time of collection, the following formula is applied:

$$C_o = Ce^{\lambda \Delta t}$$

where C_o = concentration at midpoint of collection
C = concentration at time of count
λ = ln 2/half-life (days)
Δt = time of count minus time at mid-point of collection (days)

13.5 The 2-sigma counting error expressed as a percent does not change under the extrapolation of 13.4. Therefore, the 2-sigma counting error expressed in units of concentration is:

$$\text{Error (concentration)} = \frac{\text{Error (\%)}}{100} \times C_o$$

ISOTOPIC ANALYSIS BY GAMMA RAY SPECTROSCOPY USING THALLIUM-ACTIVATED, SODIUM IODIDE CRYSTALS

1. Principle

1.1 Environmental samples contain varying amounts of naturally occurring and man-made radionuclides. Analysis of a sample's gamma ray spectrum generated by a thallium-activated, sodium iodide crystal provides a rapid method requiring minimal sample preparation for identifying and quantifying the gamma-emitting radionuclides which are present.

2. Application

2.1 This method is applicable for analyzing all types of samples which can be homogeneously placed in a standard counting geometry and contain radionuclides emitting gamma rays with energies ranging from approximately 60 thousand electron volts (60 keV) to 2 million electron volts (2 MeV).

3. Range

3.1 There is no upper range for NaI(Tl) gamma spectroscopy. The electronics have an upper limit of approximately 1×10^6 detector counts per minute (cpm). If a sample contains radionuclide concentrations, resulting in a count rate of greater than 1×10^6 cpm, then either the distance between the sample and detector is increased or an aliquot of the sample is analyzed.

4. Interferences

4.1 If the spectra for 2 or more radionuclides have an overlapping photopeak, but the remainder of their spectra are dissimilar with non-overlapping photopeaks, then the spectrum of a sample containing these nuclides can be resolved with an increase in the error terms associated with the nuclides. If the nuclides have identical or very similar spectra, the spectrum of a sample containing these nuclides cannot be directly resolved by this method.

5. Minimum detectable concentrations

5.1 The minimum detectable concentrations (MDC's) of individual radionuclides are dependent upon the following factors:

a. branching ratio of radionuclide in question
b. energy of gamma rays being emitted
c. sample size
d. the geometry in which the sample is contained
e. length of count
f. number of gamma-emitting radionuclides present in the sample.

For example, if cesium-137 is the only radionuclide present in a 3.5-liter liquid sample contained in a 4.0-liter Marinelli beaker and counted for 100 minutes, then the cesium-137 MDC is approximately 5 picocuries per liter (pCi/l).

6. Precision

6.1 The 95% confidence interval for a result obtained by gamma spectroscopy is approximately ± the MDC for samples with gamma activities close to background or ± 10% for samples with "higher" activities, i.e., the 95% confidence interval is ± the MDC or ± 10%, whichever is greater. This is based on non-overlapping gamma photopeaks. In the case of photopeak multiplets, the precision decreases with the degree of overlap.

7. Shipment and storage of samples

7.1 Samples containing or suspected of containing short-lived radionuclides require expeditious handling. Care should be exercised with all samples to assure that they are, and remain, representative and homogeneous. This may require the addition of acid to water samples to prevent dissolved nuclides from plating-out on the sample container's walls, the addition of formaldehyde to aid in the preservation of milk samples, etc.

8. Reagents

8.1 Radon-free water is used for dilution of aqueous samples to a constant volume.

9. Apparatus

9.1 Beaker, Marinelli; aluminum, 4-liter.

9.2 Can; aluminum, 200-ml.

9.3 Container; polyethylene, 400-ml.

9.4 Crystal; 4 by 4 NaI(Tl).

9.5 Planchets; stainless steel, 5-cm.

9.6 Planchets; stainless steel, 11-1/2-cm.

9.7 Spectrometer; Gamma.

9.8 Computer.

10. Procedure

10.1 Prepare homogeneous sample in a standard geometry. The standard geometries are:

a. sample contained in 5-cm diameter stainless steel planchet.
b. sample contained in 11-1/2-cm diameter stainless steel planchet.

c. aqueous sample contained in 400-ml polyethylene container.
d. aqueous sample contained in 200-ml sealed aluminum can.
e. soil sample equivalent in volume to 100 ml of water contained in 200-ml sealed aluminum can.
f. Aqueous sample (3.5-liter) contained in 4-liter aluminum Marinelli beaker.

10.2 Place sample in counting configuration and initialize gamma spectrometer to acquire gamma ray spectrum.

10.3 Print and/or store spectrum on appropriate computer compatible device.

10.4 Perform manual or computer resolution of spectrum.

11. Calibration

11.1 Bismuth-207 emits gamma rays with energies of 0.5696 MeV and 1.0634 MeV. While counting a bismuth-207 standard, adjust the amplifier gain and threshold controls until the 0.5696 MeV gamma forms a photopeak whose centroid is in channel 57 and the 1.0634 MeV gamma forms a photopeak whose centroid is in channel 106.3. The 200-channel gamma spectrometer is now calibrated from 0 to 2 MeV at 10 keV per channel.

11.2 The capability to quantitate a particular radionuclide from a gamma ray spectrum is achieved by counting a known standard of that radionuclide in each geometry used.

12. Quality Control

12.1 Each NaI(Tl) gamma spectrometer is energy-calibrated daily. Logs and quality control charts are maintained.

12.2 Known standards for quantitation are counted as needed.

12.3 Approximately 10% of all samples submitted for gamma spectrum analysis are resubmitted as blind samples. The results of these duplicate analyses are subjected to standard statistical tests. A summary of the results from the statistical tests, along with the individual analytical results, are listed in a computer printout. Results outside control limits are examined for possible remedial action.

12.4 Standard samples are received from the EMSL-LV, Quality Assurance Branch, International Atomic Energy Agency in Austria, and the World Health Organization in France. These samples are analyzed and the results are analyzed by the originating office. If the results are unsatisfactory, the reason for the anomaly is found and all results generated during the questionable time period are evaluated for possible corrective action.

13. Calculations

13.1 Nuclides are identified by the presence or absence of photopeaks and their ratios to each other.

13.2 Identified radionuclides are manually quantitated by:

a. integrating one of its photopeaks
b. subtracting the area of the photopeak beneath the continuum
c. comparing the cpm found in this net area to the cpm found in the corresponding area of a known standard of that radionuclide counted in the same geometry on the same gamma spectrometer.

13.3 A computer program, known as ALPHA M, is used to identify and quantitate radionuclides from NaI(Tl) gamma spectra. ALPHA M requires that for each radionuclide contained in the sample to be analyzed, there must be a spectrum of that radionuclide acquired from counting a standard of known activity.

13.4 The assumption made by ALPHA M is that a complex spectrum of a sample containing several radionuclides is equal to the sum of spectra of the individual radionuclides.

13.5 An example follows: Assume there is a sample containing a known quantity of iodine-131 and cesium-137. Further assume there is a standard containing a known amount of iodine-131 equal to 10 times the amount of iodine-131 contained in the sample and a second standard containing a known amount of cesium-137 equal to 20 times the amount of cesium-137 contained in the sample. Then ALPHA M assumes:

$$S = 0.1\ I + 0.2\ Cs + \varepsilon$$

where
S = sample spectrum
I = iodine-131 standard spectrum
Cs = cesium-137 standard spectrum
ε = difference between S and 0.1 I + 0.2 Cs which is primarily due to counting error

13.6 Then, if an unknown sample containing iodine-131 and cesium-137 is gamma-counted, a model of the resulting spectrum is

$$S = \beta_1\ I + \beta_2\ Cs + \varepsilon$$

where
S = unknown sample spectrum
β_1, β_2 = parameters to be estimated

13.7 There may be a change in gain or threshold between the acquisition of the known standard spectra and the acquisition of the unknown sample spectrum. To compensate for this possibility, variables for the gain and threshold, denoted G and T, respectively, are added to the model resulting in

$$S = \beta_1\ I + \beta_2\ Cs + \beta_3\ G + \beta_4\ T + \varepsilon$$

13.8 Estimates of β_1, β_2, β_3, and β_4 are obtained by applying standard weighted least squares techniques. Estimates of β_1 and β_2 yield estimates of the amount of iodine-131 and cesium-137 contained in the unknown sample since the amount of iodine-131 in the unknown sample is estimated by multiplying the activity of the iodine-131 standard by β_1. Similarly β_2 estimates the amount of cesium-137 present in the unknown sample.

13.9 Estimates of the variances associated with the amounts of iodine-131 and cesium-137 present in the unknown sample are calculated from the variances associated with β_1 and β_2 respectively. (The mathematical derivations and formulas are beyond the scope of this method. See Draper and Smith, 1966, for formulas). Thus, the errors associated with the iodine-131 and cesium-137 concentrations are statistical errors based on the least squares estimation of β_1 and β_2.

13.10 This least squares procedure can be generalized so that an unknown sample containing n nuclides can be described by the model

$$S = \beta_i N_i + \beta_2 N + \cdots + \beta_n N_n + \beta_{n+i} G + \beta_{n+2} T + \varepsilon$$

where
- S = unknown sample spectrum
- βi = least squares parameters to be estimated, i = 1, 2, ..., n+2
- N_i = individual standard spectrum of nuclide i, i = 1, ..., n
- G = gain at time of acquisition of standard spectra
- T = threshold at time of acquisition of standard spectra

13.11 With the exception of potassium-40, ALPHA M yields results in picocuries per unit of size ± the 2-sigma statistical error in picocuries per unit of size. Potassium-40 is reported as stable potassium in units of grams per unit of size ± the 2-sigma statistical error also in grams per unit of size. To extrapolate to the concentration at the time of sample collection, the following formula is applied:

$$Co = C \times e^{\lambda \Delta t}$$

where
- Co = concentration at midpoint of collection
- C = concentration at time of count
- λ = ln 2/half-life (days)
- Δt = time of count minus time at midpoint of collection (days)

14. References

14.1 Kanipe, L. G., S. K. Seale, and W. S. Liggett, "Least Squares Resolution of Gamma Ray Spectra in Environmental Monitoring." Unpublished paper prepared under project number E - AP78BDI for the Office of Research and Development, U.S. Environmental Protection Agency.

14.2 Schonfeld, E., A. H. Kibbey, and W. Davis, 1965. Determination of Nuclide Concentrations in Solutions Containing Low Levels of Radioactivity by Least Squares Resolution of the Gamma Ray Spectra, ORNL-3744. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

14.3 Schonfeld, E. 1966. ALPHA M - An Improved Computer Program for Determining Radioisotopes by Least Squares Resolution of the Gamma Ray Spectra, ORNL-3975. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

14.4 Draper, N. R. and H. Smith, Applied Regression Analysis, New York: John Wiley and Sons, Inc., 1966.

DETERMINATION OF RADIOKRYPTON, RADIOXENON, AND TRITIATED METHANE IN AIR

1 Principle

1.1 The noble gases and initiated methane are separated and collected from atmospheric samples by a series of cryogenic-gas chromatographic techniques. Water and carbon dioxide are removed by molecular sieve-13X at room temperature. Krypton, xenon, and methane are collected on charcoal at liquid nitrogen temperature. They are transferred to molecular sieve-5A where they are separated from any remaining oxygen, argon, nitrogen, and each other. The separated gases are transferred to liquid scintillation vials and counted in a liquid scintillation spectrometer.

2. Application

2.1 This method is applicable for the determination of krypton-85, -85m, -87, -88, xenon-133, -135, and tritium as methane in samples of air.

3. Range

3.1 No range has been established, however, samples have been analyzed at the 5 nCi/liter level.

4. Interference

4.1 Radon-222 will interfere with the xenon analysis. This may be eliminated through degassing of the various adsorption columns.

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.

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

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 (α) = .05

S_b = standard deviation of the background

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

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

6. Precision and accuracy

7. Shipment and storage of samples and sample stability

7.1 As most of these samples are in the form of compressed air, they cannot be shipped by air (commercial carrier).

7.2 Storage time depends on the shortest half-life of the radionuclide of interest.

8. Reagents

8.1 Acetone: commercial grade

8.2 Alcohol, ethyl: 95%

8.3 Charcoal, coconut: 16 to 20 mesh, 30 to 50 mesh

8.4 Helium: reagent grade

8.5 Liquid scintillation cocktail: Dissolve 1.5 g 2,5-diphenyloxazole (PPO) and 300 mg 1,4-bis-2-(4-methyl-5-phenyloxazole)-benzene (dimethyl-POPOP) in 800 ml spectrographic grade toluene and dilute to 1000 ml with toluene. De-gas by heating to reflux temperature.

8.6 Molecular sieve-5A: 30 to 60 mesh

8.7 Molecular sieve-13X: 1/8" x 3/16" pellets

8.8 Xenon carrier: Reagent grade

9. Apparatus

The apparatus is similar to that illustrated in Figure 15. The various components, from left to right are:

9.1 Molecular-sieve-13X: A 40 mm ID trap packed with 200 g 1/8" x 3/16" pellets of molecular sieve 13X.

9.2 Pre-cooler: 150 cm of 12-mm OD glass tubing

9.3 Pressure gauge: 0 - 760 mm of mercury

9.4 C_1: 40 mm ID trap packed with 100 g of 16 to 20 mesh charcoal

9.5 MS_1 and MS_2: 150 cm of 12-mm OD tubing packed with 30 to 60 mesh molecular sieve-5A

9.6 V-13: Two-position, 6-port valve

9.7 C_2: 20-cm length of 1/8" copper tubing packed with 0.3 g of 30 to 50 mesh activated charcoal

9.8 Liquid scintillation vial: 20-ml vial with Luer joint and valve

9.9 Manometer, digital: 0 to 100 mm of mercury

9.10 Dewar flask: 500- and 1000-ml

9.11 Electric furnace: capable of attaining 350° C

9.12 Immersion heater: 500-W

9.13 Liquid scintillation spectrometer

It is not possible to show on the line drawing all the valving and vacuum connections necessary for the operation. However, a purified helium supply is connected to the two flowmeters, and a mechanical vacuum pump is connected at both vacuum connections.

Thermistors, located in the outlets of C_1, MS_1, and MS_2, are used to detect the gas elution. The thermistor detector unbalances a Whetstone bridge circuit which in turn drives a pen on a recorder. A continuous record of the location of the various gases is thus maintained throughout the separation.

10. Procedure

10.1 De-gas all traps at 350° C and evacuate until a pressure of 10^{-} torr is obtained. Cool and fill traps with helium. Zero the thermistors with a flow of helium. Cool the pre-cooler, C_1, MS_1, and MS_2, with liquid nitrogen (LN).

10.2 Record the weight of the sample bottle and connect to the sample inlet port. Establish sample flow through mol-seive → pre-cooler → C_1 → vacuum. Adjust pressure to approximately 350 mm of mercury by means of the needle valve on sample bottle. (Reduced pressure is necessary to avoid condensation of liquid air in the system.)

10.3 Continue the transfer of sample to C_1 until the pressure drops to less than 10 mm of mercury. Close inlet valve. Remove sample bottle and reweigh (difference in weight = sample size).

10.4 Close valve C and B, open valve D, and establish helium flow (600-800 ml/min) through C_1 → thermistor 1 → vent. Remove LN from C_1 and replace with dry ice acetone slush (DIA). Continue this flow until most all the air is removed as evidenced by a return of the pen recorder to the base line (approximately 55 minutes). Close vent valve and helium flow.

10.5 Leave DIA on C_1 and establish helium flow C_1 → thermistor 1 → MS_1, → vent 2. MS_1 and MS_2 are in LN when flow is stabilized. Remove DIA from C_1 and replace with electric furnace and heat to 350° C.

10.6 Continue heating until all of the gases are transferred to MS_1. This is indicated by a return to base line by the pen on the recorder. (A shift in base line is usually noted at this point which is due to a higher temperature of the gases entering the thermistor cell.)

10.7 Close vent valve and helium vent valve. Open high vacuum valve to C_1 and continue heating until a pressure of $<10^{-4}$ torr is obtained. C_1 is ready for another run.

10.8 Establish helium flow (200 to 250 ml/min) $MS_1 \rightarrow$ thermistor 2 $\rightarrow$ vent 2. Remove LN from MS_1 and replace with a -32^{o} C alcohol bath. After 2 to 3 minutes, a sharp increase is noted on the recorder as the argon and oxygen are eluted. Continue the flow until the pen returns to the base line.

10.9 Rearrange helium flow $MS_1 \rightarrow$ thermistor 2 $\rightarrow MS_2 \rightarrow$ vent 3. Continue flow until krypton is eluted from MS_1 (approximately 12 to 14 minutes).

10.10 Quickly rearrange helium flow $MS_1 \rightarrow$ vent 2 (MS_2 and vent 3 closed). Replace the alcohol with cold water (20^{o} C) and elute the nitrogen to vent. Watch the elution of nitrogen carefully, and by rearranging the flow $MS_1 \rightarrow$ thermistor 2 $\rightarrow MS_2 \rightarrow$ vent 3, transfer the last of the nitrogen peak to MS_2 (this is mostly methane).

10.11 Place immersion heater in cold water bath and heat until carbon monoxide and xenon are transferred to MS_2 (approximately 10 minutes). Remove boiling water from MS_1.

10.12 Place a clean liquid scintillation vial and valve in position. Evacuate C_2 by heating with a heat gun until pressure is $>10^{-4}$ torr. Place LN on C_2.

10.13 Arrange helium flow $MS_1 \rightarrow MS_1 \rightarrow$ thermistor 3 $\rightarrow$ vent. Remove LN from MS_2 and replace with -32^{o} C alcohol bath. A small oxygen peak is noted in 2 to 3 minutes. When the krypton peak appears, immediately close vent 3 and open V-13, collect the krypton in C_2. When the pen on the recorder returns to the base line, close V-13, open vent 3, and allow the helium to continue to flow.

10.14 Remove the helium in C_2 by evacuating until a pressure of <0.1 mm of mercury is attained. Close vacuum valve and heat C_2 to transfer the krypton to the vial. When pressure has stabilized, record pressure and temperature. Close the Luer valve and remove valve and vial from system. Add liquid scintillation cocktail to vial and place in liquid scintillation spectrometer.

10.15 Transfer methane and xenon to liquid scintillation vials as described in 10.12, 10.13, and 10.14.

10.16 Count the separated samples for four 50-minute intervals.

11. Calibration

11.1 KRYPTON-85

Prepare counting standards by diluting a National Bureau of Standards (NBS) krypton-85 standard with xenon. (All commercial krypton currently available contains krypton-85). Add scintillation cocktail and count in liquid scintillation spectrometer (as in 10.16) to determine counting efficiency.

Counting efficiency (C.E.)

$$C.E. = \frac{cpm-bkg}{dpm(standard)}$$

where cpm = average of four 50-minute counts
bkg = background in counts per minute
dpm = activity of standard as of counting time

11.2 XENON

As the beta energy of the xenons is similar to that of krypton-85 and the beta spectrum of the krypton-85 in a liquid scintillation spectrometer is broad, the same counting efficiency is used for xenon.

Tritiated methane

11.3 Prepare counting standards by diluting a tritiated toluene standard, traceable to the NBS, and counting as in 10.16.

12. Quality Control

12.1 Every tenth sample is reanalyzed as a blind internal duplicate.

12.2 An eleventh station is rotated from sampling site to sampling site. The results, when compared to the routine station results, are used to determine sampling error.

12.3 At one-year intervals, a large sample, ~10 cubic meters, is collected and analyzed in one-cubic-meter portions to determine a standard deviation for the method.

13. Calculations

$$V_{Kr}(ml) = \frac{v \times p \times 273}{760 \times (273 + t)}$$

where V = volume of krypton in vial
v = vial volume
p = vial pressure
t = temperature (degrees Celsius)

13.2 $$\text{Krypton-85}(pCi/m^3) = \frac{1.14\ A}{2.22 \times C.E. \times V_{Kr} \times S}$$

where A = gross cpm-bkg cpm
2.22 = dpm/pCi
C.E. = fractional counting efficiency
V_{Kr} = volume krypton counted
$$S = \frac{\text{weight of sample}}{1293\ (\text{weight in grams of } 1\ m^3 \text{ dry air})}$$

13.3 XENON

$$V_{Xe}(ml) = \frac{v \times p \times 273}{760 \times (273 + t)}$$

where V_{Xe} = volume of xenon in vial
v = volume of vial
p = vial pressure
t = temperature (degrees Celsius)

13.4 $$\text{Xenon-133 or Xenon-135}(pCi/m^3) = \frac{A \times VcXe}{2.22 \times C.E. \times S \times V_{Xe}}$$

where A = gross cpm-bkg cpm
VcXe = volume Xe carrier added (ml)
2.22 = dpm/pCi
C.E. = fraction counting efficiency
S = sample size (m^3)
V_{Xe} = volume xenon counted (ml)

13.5 Tritiated methane (CH_3T)

The assumption is made that normal air contains 2 ml methane/m^3.

$$V_{CH_4} = \frac{v \times p \times 273}{760 \times (273 + t)}$$

where V_{CH_4} = volume of methane in counting vial
v = volume of vial
p = pressure in vial
t = temperature (degress Celsius)

13.6 $$\text{Tritiated methane}(pCi/m^3) = \frac{2 \times A}{2.22 \times C.E. \times V_{CHT} \times S}$$

where 2 = volume of methane in air (ml)
A = gross cpm-bkg cpm
2.22 = dpm/pCi
C.E. = fractional counting efficiency
V_{CHT} = volume of methane counted (ml)
S = sample size (m^3)

14. References

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

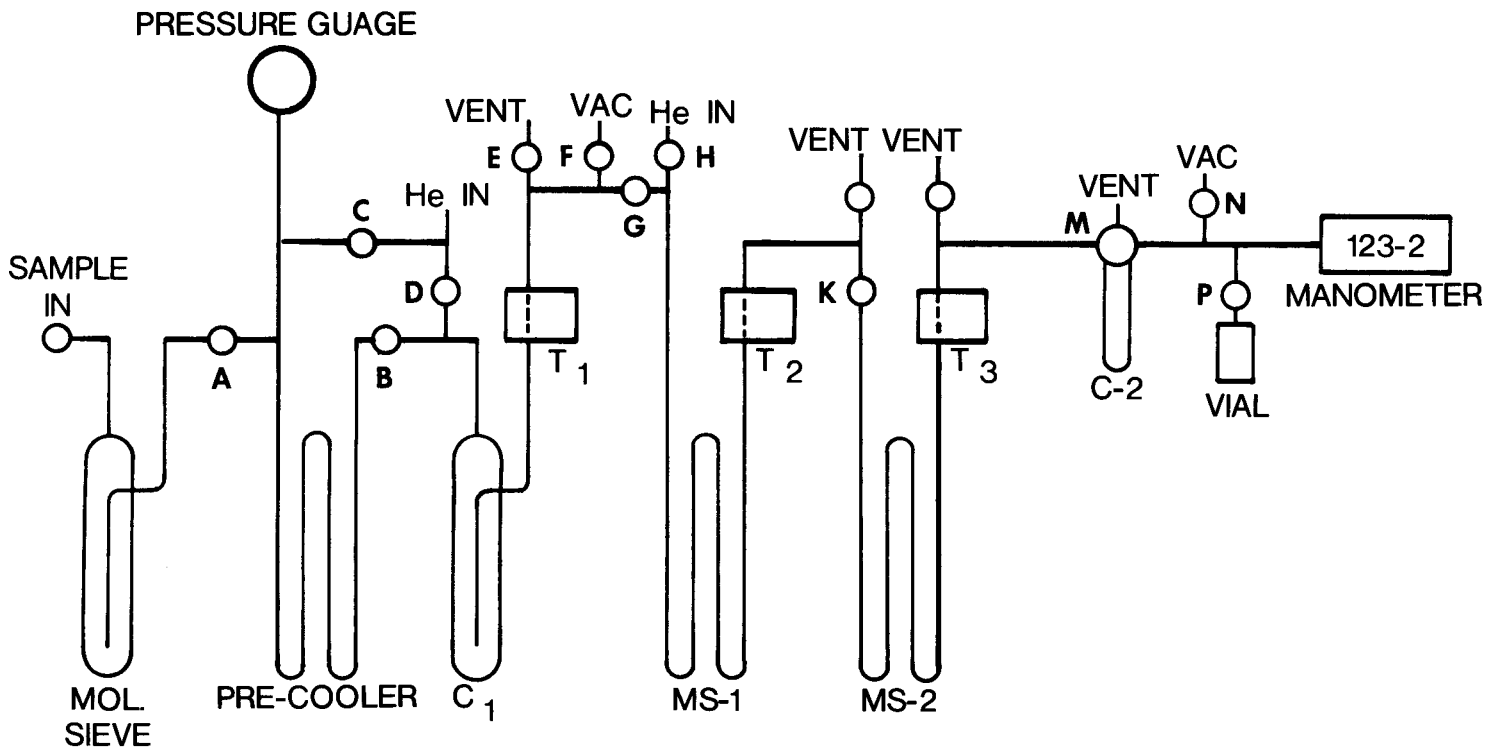

Figure 15. Noble Gas Separation Apparatus.