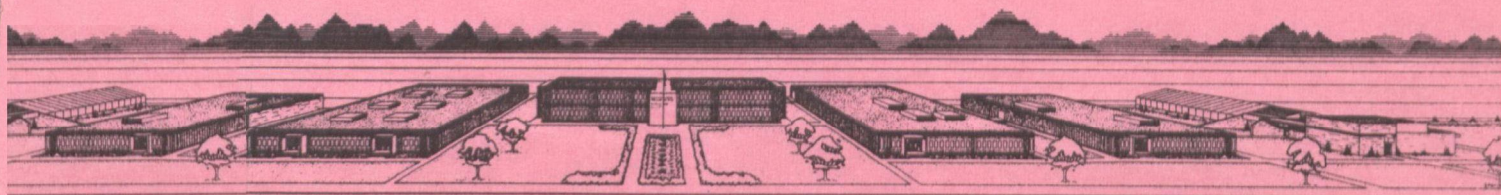


SOUTHWESTERN RADIOLOGICAL HEALTH LABORATORY
HANDBOOK OF RADIOCHEMICAL ANALYTICAL METHODS

by
Frederick B. Johns
Technical Services
Southwestern Radiological Health Laboratory

U. S. Department of Health, Education, and Welfare
Public Health Service
Environmental Health Service

March 1970
Second reprint, August 1972



SOUTHWESTERN RADIOLOGICAL HEALTH LABORATORY
HANDBOOK OF RADIOCHEMICAL ANALYTICAL METHODS

by
Frederick B. Johns
Technical Services
Southwestern Radiological Health Laboratory

U. S. Department of Health, Education, and Welfare
Public Health Service
Environmental Health Service
Environmental Control Administration
Bureau of Radiological Health

March 1970
Second reprint, August 1972

What I think chemistry is: *"I think chemistry is something that you work with a lot of things and you find out things and can make a lot of things. But sometimes things don't work and you get mad and you try to find out whats wrong. Sometimes you do things wrong like you try to make something look new but instead it truned (sic) a different color. Or you set a mixture in the freezer and it blows up. Or sometimes you go by (sic) a mixture to add so when you get home you spill it and then you start to get mad and spill all the other mixtures. So I think chemistry is just a lot of trouble."*

CHEMICAL AND ENGINEERING NEWS

NEWS Scripts

Courtesy of chemist W. S. Burnham of Duke University who came into possession of essay written by a lass named Margaret in the fifth grade at Libby Edwards School in Salt Lake City.

PREFACE

This manual is a compilation of the chemical procedures presently used at the Southwestern Radiological Health Laboratory, Las Vegas, Nevada, for the determination of stable elements and radio-nuclides in environmental and surveillance samples. It should be noted that these procedures 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.

For historical purposes, two methods for radio-strontium in milk are included since large numbers of samples were analyzed by these methods.

No listing is provided for equipment normally found in laboratories.

TABLE OF CONTENTS

	<u>page no.</u>
Rapid Ion Exchange Method for the Determination of Radiostrontium in Milk (Current Method).	1
Routine Ion Exchange Method for Strontium-89 and Strontium-90 in Milk (1966-67).	8
Determination of Strontium-89 and Strontium-90 in Whole Milk - Nitric Acid Procedure (1960-66) . . .	17
Determination of Calcium in Milk	23
Preparation of Non-Homogeneous Samples for Analysis	25
Determination of Radiostrontium in Food and Biological Samples	31
Determination of Gross Alpha and Beta Activity in Water, Total or Suspended and Dissolved Solids	36
The Determination of Radium-226 in Environmental Samples by Radon Emanation	38
Dissolution of Samples for Radium-226 Analysis . . .	42
The Determination of Radium-226 in Water Samples by Radon Emanation	45
The Analysis of Radium-226 in Soil	48
The Determination of Radium-226 in Soil Samples by Radon Emanation (A Leach Method)	51
Determination of Tritium in Water	52
Radon in Atmospheric Samples	55

TABLE OF CONTENTS

	<u>page no.</u>
A Procedure for the Separation of Radiokrypton Radioxenon, (Radon-222), Water, and Carbon Dioxide in Atmospheric Samples	58
Water and Carbon Dioxide Recovery from Molecular Sieve	68
Radon in Natural Gas.	72
Preparation of Natural Gas Samples for Analysis.	77
A Procedure for the Separation of Radioxenon and Radiokrypton from Natural Gas.	80
Analysis of Uranium by Fluorometry	83
Radiochemical Determination of Thorium in Environmental Samples	92
The Apparatus and Method for Radon Transfer,	100
Construction of Scintillation Chambers for Detecting Radon Gas.	104
APPENDIX A	110
APPENDIX B	118

FIGURES

	<u>page no.</u>
1 Ion Exchange Column, Strontium Adsorption	7
1A Ion Exchange Column, Strontium Elution	7
2 Environmental Radiation Processor, Model B	29
3 Fail Safe Circuit	30
4 Strontium Adsorption and Elution Column	35
4A Filtering Apparatus	35
5 Emanation Tube (Bubbler).	41
6 Apparatus for Radon in Air.	57
7 Apparatus for Xenon and Krypton in Air.	67
8 Radon in Natural Gas - Direct Transfer.	75
9 Radon in Natural Gas - Concentration Method	76
10 Apparatus for Separation of Xenon and Krypton in Natural Gas	82
11 Apparatus for Radon Transfer.	103
12 Lucas Scintillation Cell.	109

PHOTOGRAPHS

page no.

1	Molecular Sieve Sampler and De-gassing Cannister	71
2	Combustion Apparatus.	79

RAPID ION EXCHANGE METHOD FOR THE
DETERMINATION OF RADIOSTRONTIUM IN MILK¹

Principle of the Method:

Milk with added carriers and ethylenediaminetetraacetate (EDTA) is passed through anion and cation exchange resins; the radioiodine being adsorbed on the anion resin, the alkali metals and most alkaline earths being adsorbed on the cation resin, and the complexed calcium passing through both resins unadsorbed.

The alkaline earth metals are removed from the cation resin by elution with sodium chloride and precipitated as the carbonates. Barium is removed by chromate precipitation. Strontium-89 and strontium-90 are determined by counting twice, once after separation and again after yttrium-90 ingrowth, and strontium-89 decay. Chemical yield is determined gravimetrically.

Strontium-89 and -90 in sour milk may also be determined by this method using a batch process described on page 4 to adsorb the strontium.

Reagents^{*}:

Ammonium acetate buffer solution, pH 5.2

Ammonium hydroxide, 6N, concentrated

Complexing solution

Dowex 2-X8, 20-50 mesh

Dowex 50-X8, 50-100 mesh

Ethylenediaminetetraacetate disodium, 3%

^{*} See appendix A

¹C. Porter, et al., "Rapid Field Method for the Collection of Radionuclides from Milk," Southeastern Radiological Health Laboratory

Nitric acid, 1N
Sodium carbonate, 3N
Sodium chloride, 1.5N, 4N
Sodium chromate, 1N
Sodium hydroxide, 6N

Apparatus:

Centrifuge
Centrifuge bottles, 500-ml
Centrifuge tubes, 40-ml
Ion exchange columns*
Low-background beta counter
Membrane filters, millipore URWPO #2400
Membrane filter holders

Procedure: (See Figures 1 and 1A)

1. Add 300 ml EDTA complexing solution to one liter of cheese cloth-filtered milk and mix well. Pour the sample into funnel (Figure 1). Remove the screw cap from the bottom of cation column and allow the milk to pass through at gravity flow (approximately 100 ml/min).
2. Wash the resins with distilled water leaving enough water on the columns to keep them wet. Attach the stopcock assembly (Figure 1A) to cation column.
3. Separate and reassemble the columns (Figure 1A) discarding the anion resin. The anion resin column may be gamma scanned for the radiolodines.
4. Wash the cation column with warm (60°C) distilled water until clear to remove residual milk and then with 800 ml of 3% EDTA (pH 5.2) at a flow of 20 ml/min to remove residual calcium,

* Scientific Systems, Corp.
Baton Rouge, La. 70815

followed by 200 ml distilled water. Record the time of EDTA elution as beginning yttrium-90 ingrowth.

5. Wash adsorbed EDTA from the column with 200 ml 1.5N sodium chloride at 10 ml/min. Place 1000 ml of 4N sodium chloride in the funnel and let it flow through the column at a flow of 20 ml/min.
6. Collect the first 400 ml of eluent in a 500-ml centrifuge bottle at a flow of 20 ml/min. Allow the remaining 600 ml of 4N sodium chloride to pass through the resin to recharge at a flow of 10 ml/min. (Note 1). Discard the washings.
7. 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 (Note 2). Centrifuge and discard supernatant.
8. Dissolve the precipitate with 5 ml 1N nitric acid and transfer with distilled water to a 40-ml centrifuge tube. Add 5 ml ammonium acetate buffer (pH 2.0). Adjust pH to 4.6 with ammonium hydroxide and/or acetic acid. Heat in water bath and add 1 ml 1N sodium chromate to precipitate barium. Centrifuge and decant into a clean centrifuge tube; discard the precipitate.
9. Add 2 ml concentrated ammonium hydroxide to the supernate and swirl tube to mix well. Add 2 ml 3N sodium carbonate to reprecipitate the strontium. Heat in a water bath with stirring for 15-20 minutes. Cool, centrifuge, and discard supernate.
10. Wash precipitate twice with distilled water, centrifuge, and discard supernate after each wash.
11. Transfer the precipitate to a clean, tared planchet with a minimum of distilled water, dry, cool, and weigh. Alternately, filter through a tared membrane filter, wash well with three 10-ml portions

of water, 95% ethanol and diethyl ether. Weigh.

12. Let planchets or membrane filter set overnight and count in a low-background beta counter.
13. Recount seven days later for yttrium-90 ingrowth, and strontium-89 decay.

NOTES:

1. Anion Resin. Dowex 2-X8, 20-50 mesh, ^{-}Cl form.

Wash anion resin with distilled water until wash water checks approximately pH 5. Add resin to anion column slowly so that it fills compactly. 40 ml of resin.

Cation Resin. Dowex 50W-X8, 50-100 mesh, ^{+}Na form.

Wash 85 ml of resin (^{+}H form) with 100 ml of 4N sodium chloride eluted at 10 ml/min followed by 200 ml of 5% sodium hydroxide at 10 ml/min, then, 1000 ml of distilled water at 10 ml/min flow rate. Pack column same as anion.

2. Use an additional 1000 ml or more of distilled water to remove sodium chloride from the columns until the eluent is chloride-free (silver nitrate test for chloride).
3. An occasional sample will not precipitate. Warming the solution with stirring will usually bring down the precipitate.

Procedure for Analyses of Milk by Batch Ion Exchange:

1. Add 300 ml EDTA complexing solution to one liter of milk. Stir, and if necessary, adjust pH to 5.2 with ammonium hydroxide.
2. Add 40 ml cation resin to the solution and stir for 15 minutes on a magnetic stirrer. Allow resin to settle and decant milk into another beaker containing 40 ml of cation resin. Stir again for 15 minutes on a magnetic stirrer. Allow resin to settle and discard the milk.

3. Combine the two 40-ml portions of resin and wash several times with distilled water to remove milk and cream. Transfer the resin into an 80-ml polyethylene column (See Figure 1) attached to the top of a 45-ml polyethylene column containing 30 ml of cation resin.
4. Attach reservoir to top of columns and add 800 ml 3% EDTA pH 5.2. Let flow at 20 ml/min. Wash columns with 200 ml distilled water at the same flow rate.
5. Proceed as in step 5 of "Procedure,"

Calculations²:

$$\text{pCi } ^{90}\text{Sr}/\ell = \frac{(D)(C) - (d)(A)}{[1 + (E)(L) D -] [1 + (E)(i)] d} \times \frac{1}{(2.22)(e)(Y)(V)}$$

where:

- D = decay of ^{89}Sr from collection to time of first count^{**}
- C = net cpm of total strontium on second count
- d = decay of ^{89}Sr from collection to time of second count^{**}
- A = net cpm of total strontium on first count
- E = ratio of ^{90}Y counting efficiency to ^{90}Sr counting efficiency including self-absorption corrections
- L = ^{90}Y ingrowth from time of separation to time of second count
- i = ^{90}Y ingrowth from time of separation to time of first count
- e = counting efficiency for ^{90}Sr including self-absorption correction
- Y = fractional chemical yield
- V = sample volume in liters
- 2.22 = dpm/pCi

²V.J. Velton, "Resolution of Strontium-89 and Strontium-90 in Environmental Media by an Instrumental Technique," Nucl. Instr. Manual 42, 169 (1966).

^{**} See Appendix B

$$\text{pCi } ^{89}\text{Sr}/\ell = \frac{(A) - [1 + (i)(E)] N}{D} \times \frac{1}{(Y)(S)(V)(2.22)}$$

where:

A = net cpm total strontium on first count

i = ^{90}Y ingrowth from separation to time of first count

E = ratio of ^{90}Y counting efficiency to ^{90}Sr counting efficiency including self-absorption corrections

N = net cpm ^{90}Sr ; this is first factor in the equation for pCi $^{90}\text{Sr}/\ell$

D = decay of ^{89}Sr from collection to time of first count

Y = fractional chemical yield of strontium

S = counting efficiency for ^{89}Sr

V = sample volume in liters

2.22 = dpm/pCi

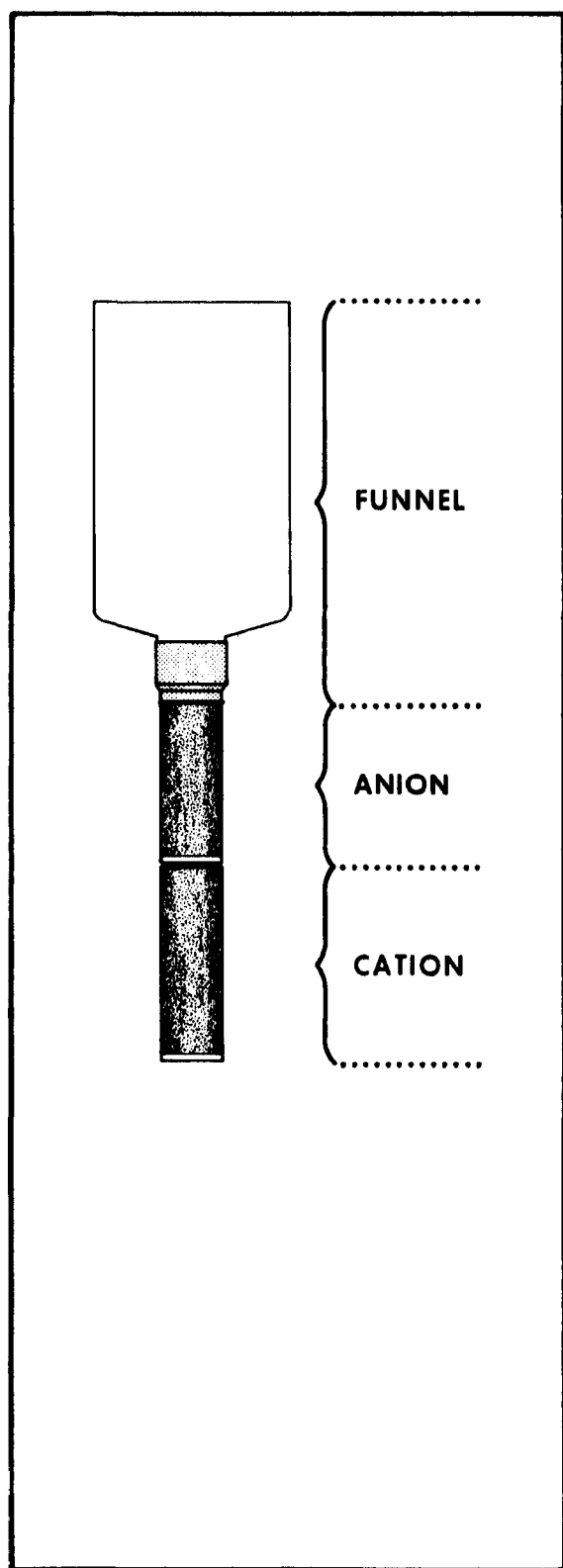


Figure 1

Ion Exchange Column, Strontium Adsorption

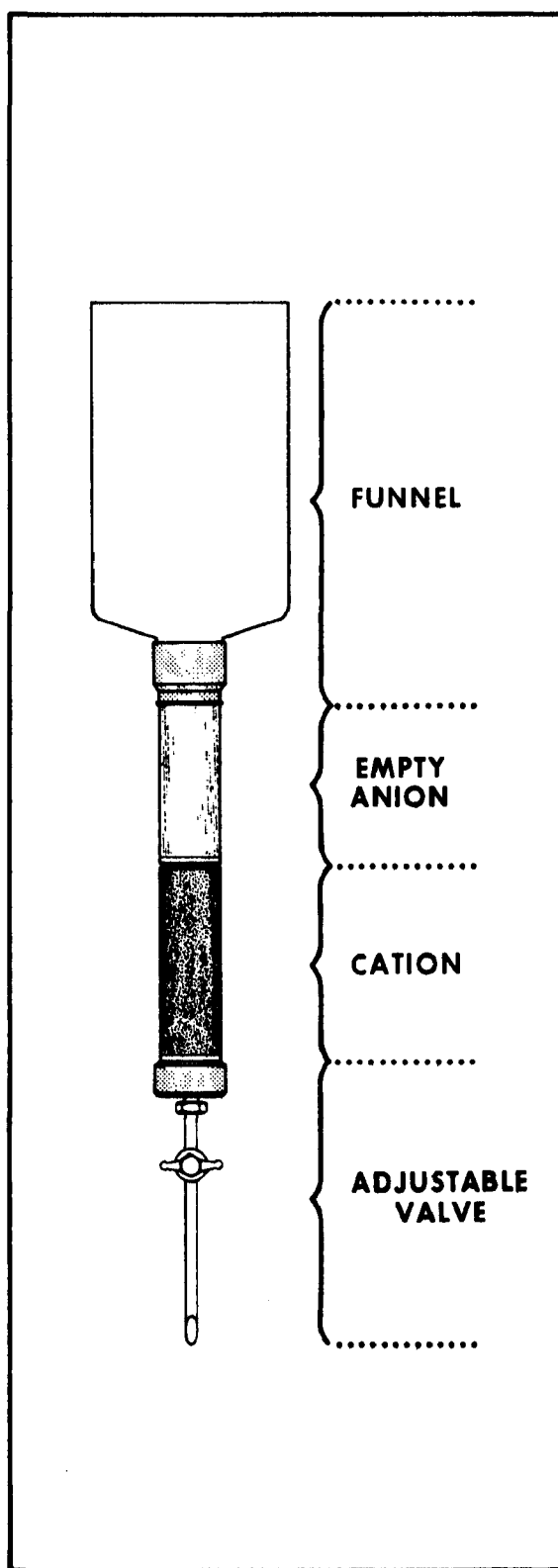


Figure 1A

Ion Exchange Column, Strontium Elution

ROUTINE ION EXCHANGE METHOD FOR
STRONTIUM-89 AND STRONTIUM-90 IN MILK

Principle of the Method:

Milk with added citrate solution containing yttrium, strontium, and barium carriers is passed successively through cation and anion exchange resin columns. Strontium, barium, and calcium are adsorbed on the cation exchange resin, and the yttrium carrier, with the yttrium-90 daughter of strontium-90, is retained on the anion exchange resin. The yttrium is eluted from the anion resin with hydrochloric acid and precipitated as the oxalate. Lanthanum-140 may be a contaminant. To remove the lanthanum contaminant, yttrium oxalate is dissolved in concentrated nitric acid and yttrium extracted from the solution into an equal volume of pre-equilibrated tributyl phosphate. The lanthanum-140 remains in the concentrated nitric acid to be discarded. Yttrium is re-extracted from the organic phase with dilute nitric acid and precipitated as the oxalate. The precipitate is weighed to determine recovery of yttrium carrier, then counted.

Calcium, strontium, and barium are eluted from the cation exchange resin with sodium chloride solution. The alkaline earth metals are precipitated as carbonates and nitrates; the latter precipitation affording a separation of strontium from calcium. Barium is removed from the strontium by chromate precipitation and strontium nitrate is counted for total radiostrontium; the yield is determined by flame spectrophotometry.

Reagents^{*}:

Ammonium acetate buffer solution

^{*} See appendix A

Ammonium hydroxide, concentrate
Barium carrier, 2.0 mg Ba^{2+} /ml
Citrate solution
Dowex 1-X8, 20-50 mesh
Dowex 50-X8, 50-100 mesh
Hydrochloric acid, 2N, 6N
Nitric acid, 0.1N, 6N, 14N, concentrate, 70% fuming
Oxalic acid, 1N
Sodium carbonate, 3N
Sodium chloride, 4N
Sodium chromate, 3N
Strontium carrier, 2.0 mg Sr^{2+} /ml
Tributyl phosphate (TBP)
Yttrium carrier, 1.0 mg Y^{3+}

Apparatus:

Ion exchange system (Kontes K-42753 or equivalent)
Low background beta counter
Spectrophotometer
Stainless steel planchets, 2-inch diameter

Procedure:

A. Preliminary Separation

1. One liter of milk (Note a) is placed in the reservoir. Yttrium, strontium, and barium carriers, 10 ml each, are added to 10 ml citrate solution and the mixture is stirred to dissolve barium citrate. The carrier-citrate solution is transferred quantitatively with a minimum amount of distilled water and the mixture is shaken vigorously. The reservoir is situated above the ion exchange columns.
2. The stopcocks on the reservoir, the anion column, and the cation

column are opened in that order. The flow rate is controlled to 10 ml/min. with the anion column stopcock (Note b). The milk is allowed to flow only until enough milk is left in the columns to cover the resins. Effluent milk is discarded. The midpoint of the elution time is recorded as the start of the yttrium-90 decay.

3. The milk reservoir is replaced with a separatory funnel containing 300 ml warm (40°C) distilled water and the columns are washed with the water to displace the milk (flow rate of 10 ml/min.). Again, the flow is stopped when the water just covers the resin. Effluent water is discarded.
4. The ion exchange columns are separated. The top cation exchange column is used for total radiostrontium determination in steps 20 to 29. The lower anion exchange column is used for the strontium-90 determination.

B. Strontium-90 Determination

5. A separatory funnel containing 100 ml 2N hydrochloric acid is attached to the top of the anion exchange column and elution is begun at 2 ml/min. Until the pH of the effluent drops to 2, as determined with pH paper on drops of effluent as they fall off the bottom of the column; the effluent is discarded. The next 10 ml of effluent are collected and the flow is stopped. The separatory funnel is removed and the resin is stirred thoroughly with a stirring rod. Washings of the rod with 2N hydrochloric acid are added to the resin. The separatory funnel is attached and elution is continued until a total of 35 ml of eluate has been collected. The eluate containing the yttrium-90 is processed as described in steps 7 to 19 below.
6. The remaining 2N hydrochloric acid is passed through the anion

exchange column at 10 ml/min. to recharge the column. The resin is washed with 100 ml water at 2 ml/min. (Note c). The resin is then ready for reuse.

7. To precipitate Y^{3+} from the eluate in step 5, 5 ml 1N oxalic acid are added and the pH of the solution is adjusted to 1.5 with concentrated ammonium hydroxide using a pH meter. The solution is stirred, heated to near boiling, cooled in an ice bath for approximately 20 min., and centrifuged; the supernatant is discarded.
8. If fresh fission products are present in the sample, steps 9 through 19 are followed. If fresh fission products are not present, the lanthanum extraction procedure (steps 9 through 14) may be omitted. In the latter instance, step 8a is performed and followed by step 15.
- 8a. The precipitate is washed with 10 ml hot distilled water and centrifuged; the supernatant is discarded. The precipitate is then dissolved in 1 ml 6N hydrochloric acid and 15 ml hot distilled water. If insoluble material remains, the solution is centrifuged and the solid residue is discarded. The supernatant is analyzed as described beginning with step 15.
9. The precipitate is dissolved in 14N nitric acid and the solution is transferred to a 60-ml separatory funnel. The centrifuge tube is washed with 10 ml pre-equilibrated tributyl phosphate (TBP); the washing is added to the separatory funnel.
10. The Y^{3+} is extracted into the TBP by vigorously shaking for two to three minutes. After phase separation, the lower, aqueous, phase is discarded.

11. The TBP is washed with 15 ml 14N nitric acid by shaking two to three minutes; the lower, aqueous, phase is discarded.
12. Repeat step 11.
13. The Y^{3+} is stripped from the TBP by vigorously shaking with 15 ml distilled water for two to three minutes. The lower, aqueous, phase is drained into a 40-ml centrifuge tube.
14. Step 13 is repeated using 10 ml 0.1N nitric acid instead of water, and the lower, aqueous, phase is added to that obtained in step 13.
15. The Y^{3+} is precipitated as the oxalate with the addition of 5 ml 1N oxalic acid followed by an adjustment of the pH to 1.5. The solution is stirred and cooled in an ice bath for approximately 20 min. After centrifugation, the supernatant is discarded.
16. The yttrium oxalate precipitate is washed twice with water and transferred onto a tared stainless steel planchet with a minimum amount of water.
17. The planchet is dried on a hot plate taking care that the precipitate is not seared.
18. After cooling, the planchet is reweighed to determine yttrium recovery.
19. The planchet is counted in a low-background beta counter.

C. Total Radiostrontium Determination

20. The alkali metals and alkaline earths are eluted from the top cation column in step 4 with 1 liter 4N sodium chloride flowing at a rate of 10 ml/min. The eluate is collected to a total volume of 1 liter.

21. The resin is washed with 500 ml distilled water; the eluate is discarded. The resin is ready for reuse.
22. The sodium chloride solution from step 20 is heated to 850-900° on a hot plate and 100 ml 3N sodium carbonate is added with stirring. The solution is removed from the hot plate and allowed to cool to room temperature. The bulk of the supernatant is decanted and the precipitate of alkaline earth carbonates is transferred, with water, to a 250-ml centrifuge bottle. The solution is centrifuged and the supernatant is discarded. The precipitate is washed twice with water.
23. The carbonate precipitate is dissolved in a minimum amount of 6N nitric acid, heating in a hot water bath if necessary to aid in the dissolution. The solution is filtered into a 40-ml graduated centrifuge tube; the filter paper and contents are discarded.
24. To the filtrate is added a sufficient volume of fuming nitric acid (Table 1) to obtain a 70% nitric acid concentration. The solution is stirred, cooled in an ice bath, and centrifuged; the supernatant is discarded.

TABLE 1

NITRIC ACID PROPORTIONS FOR STRONTIUM AND BARIUM PRECIPITATIONS

<u>To Volume of 6N Nitric Acid, ml</u>	<u>Add Amount of 90% Nitric Acid, ml</u>	<u>To Obtain Final Conc. of, %</u>
8	15	69.8
9	17	69.9
10	19	70.0
11	21	70.1
12	22	69.5
13	24	69.6
14	26	69.7
15	28	69.8

NOTE: If the volume of 6N nitric acid exceeds 15 ml, transfer to a 250-ml centrifuge bottle with 6N nitric acid and add a bulk of 90% nitric acid (150-200 ml). Cool, centrifuge, and discard supernate. Wash precipitate with concentrated nitric acid, centrifuge, and discard supernate.

25. The strontium-barium nitrate precipitate is dissolved in 5 ml water and 5 ml ammonium acetate buffer is added. The pH should be 5 as determined with pH paper.
26. The solution is heated in a water bath and 1 ml 3N sodium chromate is added with stirring. The solution is centrifuged; the supernatant being decanted into a clean 40-ml centrifuge tube; the barium chromate precipitate being discarded.
27. Thirty ml fuming nitric acid are added to the supernatant from step 26. The solution is cooled, centrifuged, and decanted. The time of decantation is recorded as start of yttrium-90 ingrowth.
28. The precipitate is dissolved in a minimum amount of water and transferred quantitatively onto a 2-inch stainless steel planchet. The planchet is evaporated to dryness on a hot plate, cooled, and counted in a low-background beta counter.
29. The residue on the planchet is dissolved in water and transferred quantitatively to a 250-ml volumetric flask. The solution is diluted to the mark, shaken well, and 20 ml are pipetted into a 100-ml volumetric flask. The latter solution is diluted to the mark with water and submitted for strontium yield determination by atomic absorption.

Calculations:

$$^{90}\text{Sr}: \text{ pCi/l} = \frac{C-B}{(2.22)(E)(Y)(V)(D)(I)}$$

where C = cpm obtained by counting yttrium oxalate

B = cpm background

2.22 = dpm/pCi

E = counting efficiency for yttrium-90 in $\frac{\text{cpm}}{\text{dpm}}$

Y = fractional yield of yttrium carrier

V = volume of sample in liters

D = correction factor for yttrium-90 decay ($e^{-\lambda t}$)

where t is the time from the midpoint of the elution time to the time of counting, and λ is the decay constant for yttrium-90.

I = correction factor for degree of yttrium-90

ingrowth ($1-e^{-\lambda t}$) where t is the time from the collection of the milk sample to the time of passage through the column.

$$^{89}\text{Sr}: \text{ pCi/l} = \frac{1}{(2.22)(E)(D)} \frac{C-B}{(Y)(V)} - (2.22)(S)(F) - (2.22)(S)(G)(I)$$

where 2.22 = dpm/pCi

E = fractional counting efficiency for strontium-89

D = correction factor for strontium-89 decay ($e^{-\lambda t}$)

where t is the time from sample collection to time of counting, and λ is the decay constant for strontium-89.

C = cpm obtained by counting strontium nitrate

B = cpm background

Y = fractional yield of strontium carrier

V = volume of milk sample

S = pCi/l strontium-90 as calculated above

F = fractional counting efficiency for strontium-90 including the self-absorption factor

G = fractional counting efficiency for strontium-90
I = correction factor for yttrium-90 ingrowth ($1 - e^{-\lambda t}$),
where t is the time from the last decantation of
nitric acid from the strontium nitrate precipitate
to the time of counting.

NOTES:

- a. The milk must be reasonably homogeneous, preserved with formaldehyde, and refrigerated (approximately 0°C) for two weeks to allow the yttrium-90 to come to equilibrium with the strontium-90.
- b. If the stoppers in the cation and the anion columns are air-tight, flow can be adjusted using only the anion column stopcock.
- c. Trapped milk particles can be removed by backwashing with water or by slurring the resin with water.

DETERMINATION OF STRONTIUM-89 AND STRONTIUM-90 IN WHOLE MILK

NITRIC ACID PROCEDURE

(1960-66)

Principle of the Method:

After the addition of a strontium carrier, the milk proteins are precipitated with trichloroacetic acid. Following filtration, excess oxalic acid is added to the filtrate and the alkaline earths are precipitated as the oxalates at pH 3.0. The oxalates are then converted to the nitrates. Calcium and strontium are separated by differences in solubility. The strontium is scavenged with barium, iron, and rare earth carriers. After a final nitric acid extraction of yttrium-90, the strontium precipitate is stored for a minimum of one week to allow for yttrium ingrowth. After this period, the strontium is re-precipitated with 70% nitric acid, and yttrium is recovered in the supernatant. Both fractions are mounted on a planchet and counted for beta activity.

The strontium-89 activity is the calculated difference between total strontium activity and the strontium-90 (as yttrium-90 activity).

Reagents * :

Acetic acid, 1.5N

Ammonium acetate, 3N

Ammonium acetate buffer, pH 5

Ammonium hydroxide, 1N, 6N, concentrated

Barium carrier, 5 mg Ba²⁺/ml

Bromocresol green (B.C.) indicator

* See appendix A

Hydrochloric acid, 0.5N, concentrated
Hydrogen peroxide, 30%
Mixed rare earth carrier
Nitric acid, 0.5N, 1N, 3N, concentrated, 90% fuming
Oxalic acid, saturated at room temperature
Sodium chromate, 1N
Sodium carbonate, 3N
Strontium carrier, 8 mg Sr^{2+} /ml
Trichloroacetic acid, 50%

Apparatus:

Buchner funnel
Filter sticks, medium porosity
Low background beta counter
Stainless steel planchets, 2" diameter

Procedure:

1. Place a 1000-ml aliquot of sample into a 2000-ml beaker. Add strontium carrier (80.0 mg) and stir solution thoroughly.
2. Add 300 ml of 50% trichloroacetic acid (TCA) to the solution with stirring. Filter the solution through Whatman # 2 filter paper into a Buchner funnel and collect filtrate in a 3000-ml flask. Wash precipitate with three portions of distilled water.
3. Transfer filtrate into a 2000-ml beaker and rinse the flask with distilled water. Add 125 ml of saturated oxalic acid to the solution and thoroughly mix the solution. Adjust pH to 3.0 with concentrated ammonium hydroxide, using a pH meter. Allow 5 to 6 hours for precipitate to settle.
4. Aspirate the supernatant through a medium porosity filter stick. Wash the beaker and precipitate with three portions of distilled water.

5. Transfer precipitate to a 250-ml beaker with concentrated nitric acid, the filter stick being placed in the beaker. Heat the beaker on a hot plate until precipitate separates from the filter stick. Rinse the filter stick inside and out with concentrated nitric acid and remove.
6. Evaporate the solution to near dryness. Add 50 ml of concentrated nitric acid and evaporate to near dryness. (Repeat until the residue is colorless.)
7. Transfer the residue to a 40-ml centrifuge tube with a minimum of concentrated nitric acid, and then cool the solution overnight in refrigerator. Centrifuge at 1500-1800 rpm for ten minutes and discard the supernatant.
8. Dissolve the precipitate in 5 ml of 3N nitric acid and add 10 ml of fuming nitric acid. Centrifuge the mixture and discard the supernatant.
9. Dissolve precipitate in 5 ml water. Add three drops of bromocresol green indicator to the solution. Add 6N ammonium hydroxide until the color changes from yellow to blue. Use 0.5N nitric acid to back titrate until the solution barely turns yellow. Add 5 ml of ammonium acetate buffer solution and 1.0 ml of barium carrier. Heat solution in a water bath and add 1.0 ml of 0.25N sodium chromate. Heat solution until a definite barium chromate precipitate is noticed. Cool solution and filter through a Whatman # 42 filter paper into a 250-ml beaker. Wash precipitate with distilled water.
10. Add 5 drops of mixed rare earth carrier to the filtrate, 2 drops hydrochloric acid, and 5 drops of 30% hydrogen peroxide. Warm

The solution and add concentrated ammonium hydroxide until a precipitate forms. Filter the solution through a Whatman # 42 filter paper and wash with distilled water.

11. Allow the filtrate to evaporate to approximately 10 ml and transfer to a 40-ml centrifuge tube with concentrated ammonium hydroxide. Add 5 ml concentrated ammonium hydroxide and 2 ml 3N sodium carbonate. Mix the solution, cool, and centrifuge. Discard the supernatant.
12. Dissolve precipitate in a maximum of 6 ml of 3N nitric acid. Add 30 ml of fuming nitric acid to the solution. Cool the solution and centrifuge; discard the supernatant. Record time and date as T_1 (start of yttrium ingrowth). Store the precipitate for a minimum of one week.
13. After a suitable ingrowth period, dissolve the strontium nitrate precipitate with 5 ml water.
14. Add 30 ml of fuming nitric acid and cool the solution in a water bath. Record time and date as T_2 (completion of ingrowth).
15. Centrifuge the solution and decant the supernatant into a 250-ml beaker.
16. Dissolve the residue in 6 ml of distilled water and repeat steps 15 and 16, combining the supernatants.
17. Evaporate supernatant to a small volume and transfer with 3N nitric acid to a stainless steel planchet. Evaporate the solution to dryness and submit for beta counting of yttrium-90.
18. Transfer the precipitate with distilled water into a tared planchet and evaporate to dryness. Determine the weight of the residue for self-absorption correction and submit for beta counting of total strontium-89 and -90 (Note b).

Calculations:

$$T = \frac{C}{(2.22) (E) (Y) (V)}$$

$$N = \frac{n}{(2.22) (e) (Y) (I) (D) (V)}$$

$$S = \frac{T - N}{(d)}$$

Where

T = pCi/l radiostrontium

C - cpm total radiostrontium counted

2.22 = dpm/pCi

E = counting efficiency for strontium-90 including self-absorption

Y = chemical yield for strontium

V - volume of sample taken in liters

N = pCi/l strontium-90

n = cpm yttrium-90 counted

e = counting efficiency for yttrium-90

I = ingrowth of yttrium-90 from T₁ to T₂

D = decay of yttrium-90 from T₂ to time of count

S = pCi/l strontium-89

d = decay of strontium-89 from time of collection to time of count

NOTES:

- a. Total radiostrontium may be determined at this point.
- b. Before planchets are submitted to the counting room, they must be absolutely dry. In some cases where liquid residue the planchet is placed in a muffle furnace at 400°C for thirty minutes.

References:

1. Murthy, G. K., et al., "A Method for the Determination of Radio-nuclides in Milk Ash," Dairy Science, Vol. 42, pp. 1276-87 (1959).
2. Murthy, G. K., et al., "A Method for the Elimination of Ashing in Strontium-90 Determination of Milk," Dairy Science, Vol. 43, pp. 151-4 (1960).

DETERMINATION OF CALCIUM IN MILK

Principle of the Method:

This method describes a procedure for the determination of calcium in milk. An aliquot is diluted with water, hydroxylamine hydrochloride and potassium hydroxide are added, and the resulting solution is titrated with disodium ethylenediaminetetraacetate, using Cal-Red^R as an indicator.

Reagents^{*}:

Ethylenediaminetetraacetate (EDTA, disodium 0.004N)

Hydroxylamine hydrochloride, 5%

Indicator "Cal-Red" Indicator Dilute^{**}

Potassium hydroxide, 5N

Apparatus:

Flask, Erlenmeyer, 125-ml

Microburet, 5-ml, calibrated in 0.01

Pipet, 5-ml, 10-ml

Stirrer, magnetic

Procedure:

1. Pipet 10 ml of milk into a 125-ml Erlenmeyer flask, and dilute with 50 ml distilled water.
2. Add 5 ml of 5% hydroxylamine hydrochloride and 5 ml 5N potassium hydroxide.

^{*} See appendix A

^{**} Trade Mark registered, Scientific Services Laboratories, U. S. Patent Office, Washington, D. C.

3. Add Teflon stir bar and mix well, let stand a minimum of three minutes (maximum of five minutes).
4. Add approximately 0.1 g of "Cal-Red" indicator, titrate immediately with 0.004N EDTA. At the end point, the solution will change from a lavender color to baby blue.

Calculation:

$$\text{Ca g/liter} = \frac{A \times B \times C}{D}$$

where A = equivalent wt for calcium

B = volume of EDTA ml

C = normality of EDTA (eq/liter)

D = sample volume (ml)

PREPARATION OF NON HOMOGENEOUS SAMPLES FOR ANALYSIS

Principle of the Method:

This procedure describes methods for the grinding, blending, and ashing of food, bone, tissue, vegetation, and rumen samples. The food is ground and blended in an Environmental Residue Processing Apparatus, an apparatus built at SWRHL to combine grinding and blending of total diet samples. The other biological samples are cleaned and ashed to remove all traces of organics.

Reagents^{*}:

Formalin

Apparatus:

Balance, 10 kg

Environmental Residue Processing Apparatus (Figures 2 and 3)

Marinelli beaker, 3 1/2-liter

Muffle furnace

Porcelain Casserole, 1800-ml

Wiley Mill

Procedure:

A. Institutional Surveillance Diet Network Samples

1. Obtain weights of all containers with samples.
2. Add the liquid fractions to the blender. (Figure 2)
3. Start blender/grinder and add solid portion, checking and removing inedible items (note these items).

^{*} See appendix A

4. Allow sample to circulate for 10 minutes - add 10 ml formalin to total sample.
5. Weigh the empty containers to obtain net weights of liquid and solid portion.
6. Stop blender and record volume of sample.
7. Transfer 3 1/2 liters of blended sample to a Marinelli beaker, and submit for gamma spectroscopy analysis.
8. The remaining blended sample is transferred to tared 1800-ml casseroles and reweighed. Proceed to step C-1.
9. Clean the blender/grinder with soap and water. (Notes 1, 2, and 3.)

B. Bone, Tissue, Vegetation, and Rumen Samples

1. Remove all visible foreign matter from samples and either by sawing or compaction, transfer all of the sample to tared 1800-ml casseroles and weigh. Proceed to step C-1.

C. Ashing

1. Place the casseroles (from step A-8 and B-1) in muffle furnace and dry at 150°C overnight or longer.
2. Increase the temperature, common sense is best indicator, gradually until 600°C is reached. Hold at this temperature until the ash is powdery and light gray or tan in color. Prolonged ignition or over-heating of high phosphate sample (eggs, pork, beef) should be avoided as a phosphate "glass" which is difficult to dissolve tends to form. An occasional grinding with a pestle will speed up the ashing.
3. After ashing is complete, turn off furnace and allow to cool,

4. Weigh and grind the food ash with a mortar and pestle, bone ash in the Wiley Mill. Combine the food ash and regrind.

NOTES:

1. Do not allow pump to operate without water or sample in the reservoir. The rubber impeller is subject to severe wear when running dry.
2. A small quantity of water will remain in the lower parts of the apparatus. To remove before operation, remove drain plug and drain into a beaker.
3. The fail-safe circuit (Figure 3) is designed to turn off the pump in case the thermal overload breaker on the disposal unit trips. When this happens, turn off switch, check the disposal blade for jamming, turn on switch, and push the over-load button located on the disposal unit. This will start the apparatus again.

Calculations:

- A. To obtain total ash weight of the food sample:

$$\text{ash, g} = A \left(\frac{B}{B - 3.5} \right)$$

where A = weight of combined ash, g

B = volume of total blended sample, l

3.5 = volume of Marinelli beaker, l

B. To obtain % ash weight for food:

$$\text{ash \% w} = \frac{C}{D \times 10}$$

where C = total ash weight, g

D = total sample weight, kg

C. To obtain % ash weight for bone, tissue, etc.:

$$\text{ash \% w} = \frac{C}{E} \times 100$$

where C = total ash weight, g

E = total sample weight, g

MODEL ERP-B

WATER TAP

DISPOSAL UNIT FEED

ACCESS LID

CONTROL SWITCH

OVERLOAD RESET

SAMPLING VALVE

RESERVOIR

SEWER CONNECTION

DRAIN PLUG

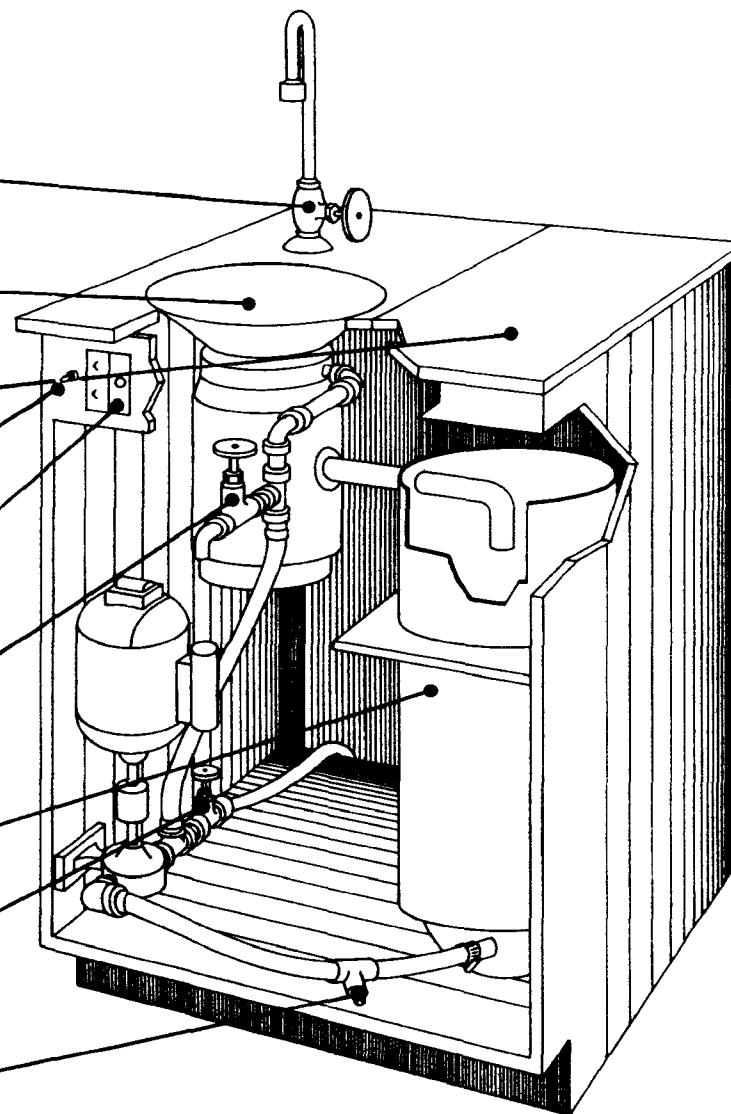
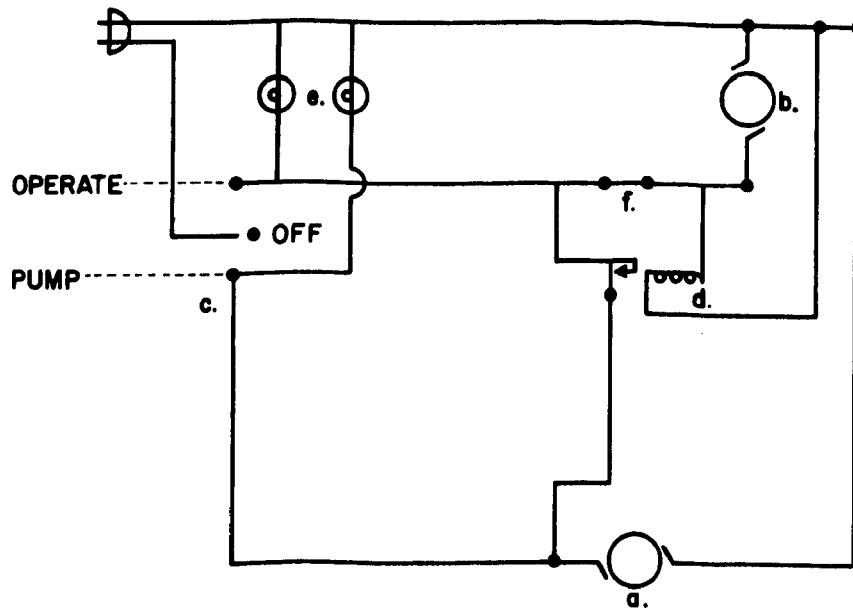


Figure 2
Environmental Radiation Processor, Model B

FAIL-SAFE CIRCUIT



- a. 1/3 hp CAPACITOR START MOTOR _____
- b. YOUNGSTOWN FOOD WASTE DISPOSAL _____
- c. S.P.D.T. OFF POSITION BAT SWITCH _____
- d. S.P.S.T. RELAY _____
- e. PILOT LIGHTS _____
- f. THERMAL SWITCH _____

Figure 3
Fail Safe Circuit

DETERMINATION OF RADIOSTRONTIUM
IN FOOD AND BIOLOGICAL SAMPLES

Principle of the Method:

This method describes a procedure for the determination of strontium-89 and -90 in various biological samples. The ash is fused as a carbonate, the strontium-calcium carbonates are dissolved in hydrochloric acid, complexed with disodium ethylenediaminetetraacetate (EDTA), passed through an ion exchange column where the strontium is adsorbed, and the complexed calcium passes through. The strontium is eluted, precipitated as a carbonate, and mounted on a planchet for beta counting. Chemical yield is determined gravimetrically.

Reagents*:

Ammonium hydroxide, concentrated
Barium carrier
Calcium carrier
Ethylenediaminetetraacetate disodium, 6%, 2%
Hydrochloric acid, 6N, 1.5N
Sodium acetate buffer solution
Sodium carbonate, anhydrous, 3N
Sodium chloride
Sodium hydroxide pellets
Strontium carrier

Apparatus:

Crucible/cover, nickel, 250-ml
Bath, cooling

*See appendix A

pH meter

Funnel, separatory, graduated, 1000-ml

Column, 2.5 cm I. D. (Fig. 4), 40 ml resin

Filter paper, milipore #URNPO 2400

Procedure A, Food, Bone, Vegetation or Tissue:

TABLE 2 - Various Sample Types, Sample Size and Carriers				
Type	Sample Size, g	Strontium, ml	Carrier Calcium (2M)	Ba (5 mg)
Food	10	2	--	1
Bone	2	2	--	1
Veg.	2 or 5	2	1	1
Tissue	2	2	1	1

1. Weigh necessary sample (Table 2) and place in a 250-ml nickel crucible, add carriers as indicated and 50 g sodium hydroxide pellets. Mix and cover.
2. Fuse over burner for 30 minutes, slowly add 5 g anhydrous sodium carbonate, swirl, and continue fusion for thirty minutes.
3. Transfer crucible with cover to cold water bath to crack mixture.
4. When cold, add 200 ml hot distilled water, boil to disintegrate the fused mixture.
5. Cool and transfer to 250-ml centrifuge tube. Centrifuge, discard supernatant solution. Repeat twice with 200-ml portion of hot distilled water.
6. Add 20 ml 6N hydrochloric acid and with gentle heat dissolve the residue. Add 100 ml distilled water. (Note 1.)

7. 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.
8. Filter (Fig. 4A) collect the filtrate and adjust to pH 4.6 with ammonium hydroxide. Add 20 ml buffer solution. Readjust pH to 4.6.
9. Quantitatively transfer to the 1000-ml graduated cylinder and dilute to 1000 ml with distilled water.
10. Adjust solution flow through resin column to 10 ml/min. Stop flow when just enough solution remains to cover resin. Discard effluent.
11. Adjust 600 ml 2% EDTA to pH 5.1 with ammonium hydroxide, place in reservoir, and let flow at 20 ml/min. Record time at end of elution as T-1 (beginning of yttrium-90 ingrowth). Wash column with 200 ml distilled water at a flow of 20 ml/min. Discard washings.
12. Place 460 ml 1.5N hydrochloric acid in reservoir, and elute at a flow rate of 8 ml per minute. Discard first 60 ml of effluent. Collect in an 800-ml beaker the next 400 ml which contains the strontium fraction.
13. Regenerate resin with 600 ml 4N sodium chloride followed by 1000 ml distilled water, both at a flow rate of 10 ml per minute.
14. Add 200 ml concentrated ammonium hydroxide to the strontium fraction with stirring. Slowly add 10 ml 3N sodium carbonate, and stir 30 minutes.
15. Transfer to 500-ml centrifuge tube in 2 or 3 portions and centrifuge, discarding supernate each time.
16. Wash with distilled water twice and transfer precipitate to tared planchet. Dry planchet, and reweigh for yield and self-absorption. Alternately, filter through tared membrane filter, wash well with 3-10 ml portions of water, 95% ethanol and diethyl ether. Weigh.
17. Let planchets or membrane filter set overnight and count in a low-background beta counter.

18. Recount seven days later for yttrium-90 ingrowth.

NOTE:

1. If insoluble residue (silica) is present, filter, wash residue twice with 100-ml portions of distilled water and add to filtered solution; discard residual.

Procedure B, Water:

Add 33.3 g EDTA, 2 ml strontium carrier, 1 ml barium and calcium carriers to 1000 ml of water sample. Adjust pH to 4.6 with ammonium hydroxide and proceed as in step A-8.

Calculation:

See Calculations, "Rapid Ion Exchange Determination of Radiostrontium in Milk," pp. 5 and 6.

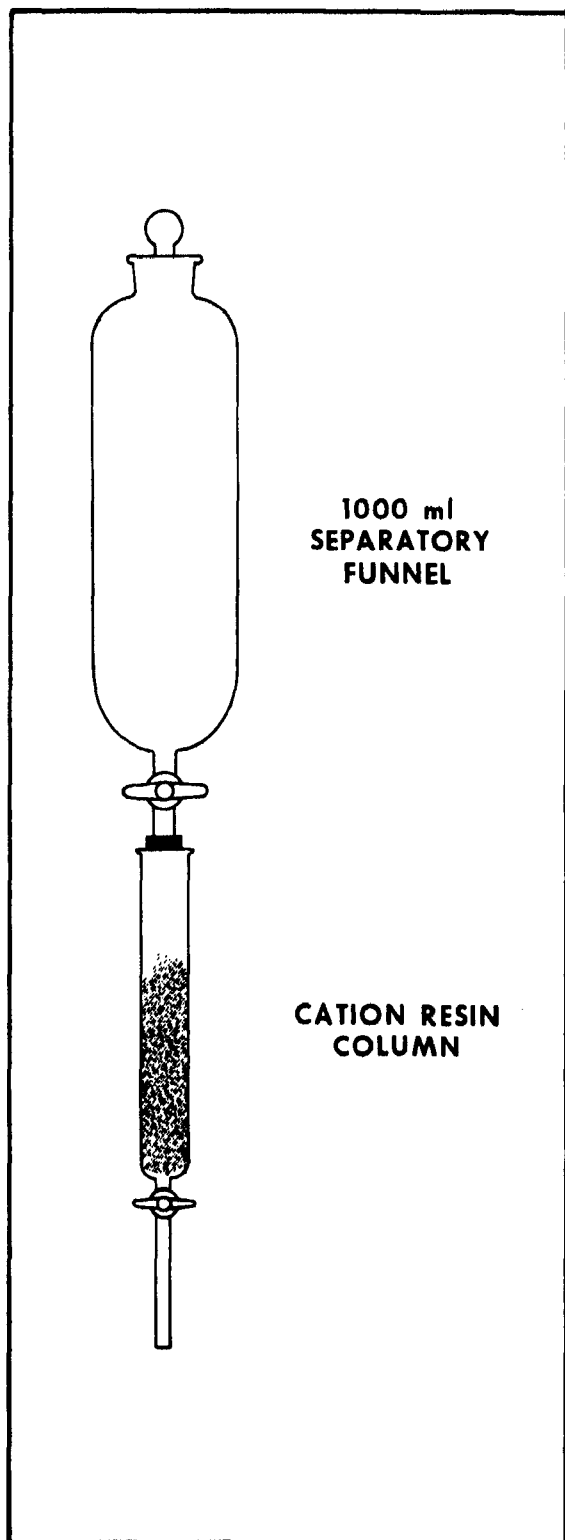


Figure 4
Strontium Adsorption and Elution Column

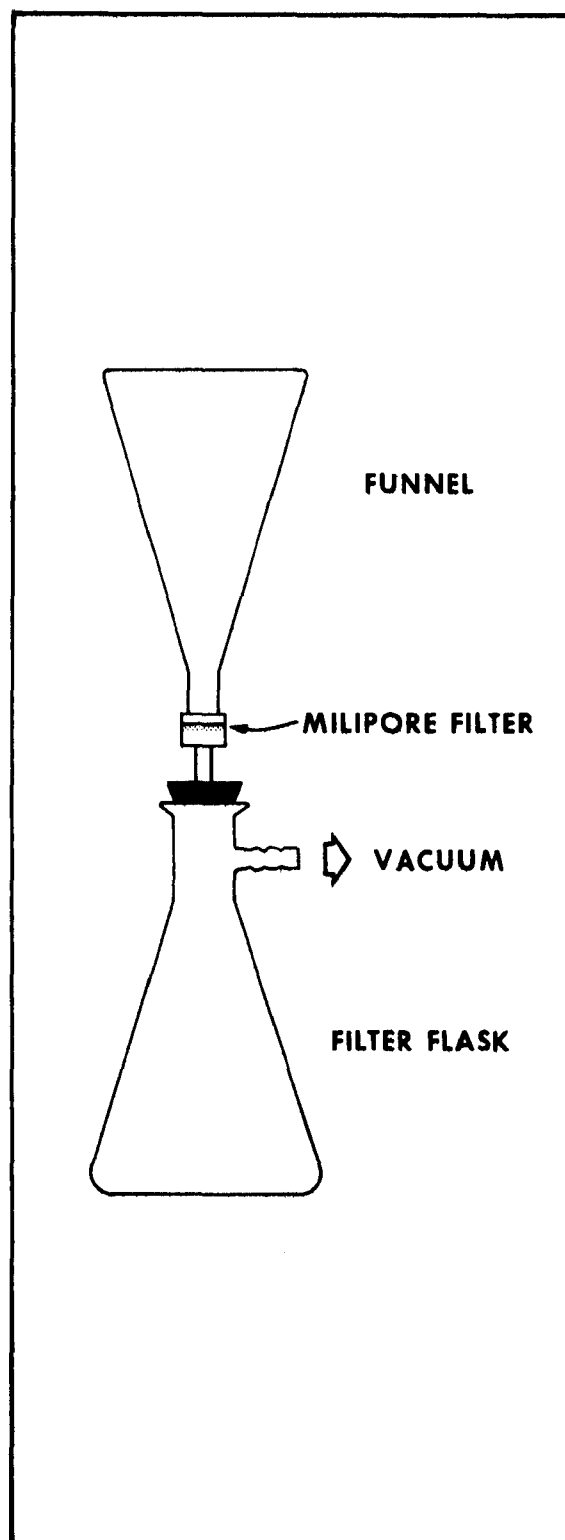


Figure 4A
Filtering Apparatus

DETERMINATION OF GROSS ALPHA AND BETA ACTIVITY IN WATER

(TOTAL, OR SUSPENDED AND DISSOLVED SOLIDS)*

Principle of the Method:

This method describes procedures for the determination of gross alpha and beta activity in natural waters. This activity is not indicative of any specific nuclide; however, it does provide an index to the radioactive contamination of the sample.

Reagents**:

Ethyl alcohol, 95%

Nitric acid, 3N, concentrated

Procedure:

1. Filter a 1000-ml aliquot of the sample through a 9 cm Buchner funnel using a 9 cm diameter Whatman #42 filter paper. Collect the filtrate in a 2000-ml filter flask and save for step 3.
2. Place filter paper containing suspended solids in a tared planchet, saturate with ethyl alcohol and ignite. Flame the planchet to a dull red, cool, weigh for self-absorption correction and submit for alpha and beta counting.
3. Transfer a 250-ml aliquot of the filtrate from step 1, unfiltered sample, to a 400-ml beaker, add 10 ml nitric acid (concentrated) and evaporate to near dryness. Quantitatively transfer to a tared planchet using 3N nitric acid. Flame planchet to a dull red, cool, weigh for self-absorption correction, and submit for alpha and beta counting.

* Standard Methods for the Examination of Water and Waste Water, Twelfth Edition.

** See appendix A

Calculations:

pCi alpha or beta/l =

(Dissolved Solids)

(Suspended Solids)

$$\frac{\text{cpm}}{\text{eff} \times 2.22 \times \text{sample volume}} + \frac{\text{cpm}}{\text{eff} \times 2.22 \times \text{sample volume}}$$

eff = beta counting efficiency as determined using a strontium-90
-yttrium-90 equilibrium standard including self-absorption
correction or alpha counting efficiency using plutonium-239.

NOTES:

1. If radium-226 and/or strontium-90 are requested by the originator of the sample, save the unused portion until the gross activity measurements have been completed.
2. For drinking water, if the total alpha activity is greater than 3 pCi/liter, radium-226 content must be determined. And, if the total beta activity is greater than 10 pCi/liter, strontium-90 must be determined.
3. Volumes smaller than 250 ml may be used if weight is too large for efficient counting.

THE DETERMINATION OF RADIUM-226
IN ENVIRONMENTAL SAMPLES BY RADON EMANATION **

Principle of the Method:

A weighed aliquot of sample ash is digested with 16N nitric acid and 30% hydrogen peroxide. After addition of barium carrier, the sample is precipitated as a carbonate with ammonium carbonate. The carbonate precipitate is dissolved with 3N nitric acid and the sample is precipitated as a chromate using ammonium chromate. The chromate precipitate is dissolved with 12N hydrochloric acid, and re-precipitated as a chloride with hydrochloric acid-ether solution. The chloride precipitate is readily soluble in less than 10 ml water. The solution is then transferred to an emanation tube for twenty-eight days.

Reagents * :

Acetic acid, 6N

Alcohol-hydrochloric acid, 10 ml hydrochloric acid/100 ml
absolute alcohol

Ammonium acetate, 6N

Ammonium carbonate, saturated solution

Ammonium carbonate wash solution

Ammonium dichromate, 0.1M, 1.0M

Ammonium hydroxide, 6N, 15N

Barium carrier, 1 mg barium/ml, 10 mg barium/ml

Hydrochloric acid, 12N

Hydrochloric acid-ether

Hydrogen peroxide, 30%w

Nitric acid, 3N, 16N

* See appendix A

** Unpublished work of E. Halker, D. Moden and F. Johns

Apparatus:

Bath, ice

pH meter

Tube, immersion, Corning #39535, 20M or equivalent

Tube, emanation (Fig. 5)

Procedure:

(See "Dissolution of Samples for Radium-226 Analysis")

1. Weigh on an analytical balance a 5-gram portion of sample ash into a 400-ml beaker.
2. Digest with 16N nitric acid and 30% hydrogen peroxide, evaporate to near dryness, repeat the digestion if necessary until sample is in solution. (Do not allow sample to evaporate to dryness.)
3. Increase volume to at least 150 ml with distilled water, heat and add a few ml 16N nitric acid to insure complete solution of the sample. (Some flocculant precipitate of phosphates may be present and may be disregarded at this time.)
4. Add 5 mg barium carrier and adjust the pH to greater than 7.0 with ammonium hydroxide. Add 30 ml saturated solution of ammonium carbonate, allow precipitate to settle for 30 minutes. Filter using immersion tube, or centrifuge using a 250-ml centrifuge bottle. Discard the filtrate and wash the precipitate several times with hot ammonium carbonate wash solution.
5. Dissolve the carbonate precipitate with 3N nitric acid, wash the filter stick and walls of the beaker with 3N nitric acid.
6. Add 100 mg of barium carrier, increase the volume of the sample to 150 ml with distilled water, heat on the hot plate until the sample is in solution.
7. Adjust the pH to 4.2 to 4.6 with 6N ammonium hydroxide or 3N

nitric acid. Add 3 ml 6N acetic acid, 10 ml ammonium acetate, and slowly with stirring, add 10 ml 1.0M ammonium dichromate solution pH 6.5. Allow the chromate precipitate to settle for 30 minutes; filter, using an immersion stick, or centrifuge using a 250-ml centrifuge bottle. Discard the filtrate and wash the precipitate with 0.1M solution of ammonium dichromate pH 6.5.

8. Dissolve the precipitate with 12N hydrochloric acid, wash the sides of the beaker and the filter stick with 12N hydrochloric acid. Heat on the hot plate and add more hydrochloric if necessary to insure complete solution of the sample.
9. Remove the sample from the hot plate and chill in an ice bath. In a hood, add 30 ml hydrochloric acid-ether solution^{*}; allow sample to set in ice bath for 20 minutes; filter, using a filter stick that has been washed with hydrochloric acid-ether solution. Discard the filtrate and wash the barium (radium) chloride precipitate with absolute alcohol-hydrochloric acid solution.
10. Dissolve the barium (radium) chloride with a maximum of 8 ml of distilled water. Transfer the sample to an emanation tube, (Fig. 5) washing beaker and funnel with a maximum of 4 ml of distilled water. Final volume should be a minimum of 10 ml; maximum of 12 ml. Seal and allow to ingrow for 28 days. (See "The Apparatus and Method for Radon Transfer" for de-emanation of radon.)

^{*}Caution, highly flammable.

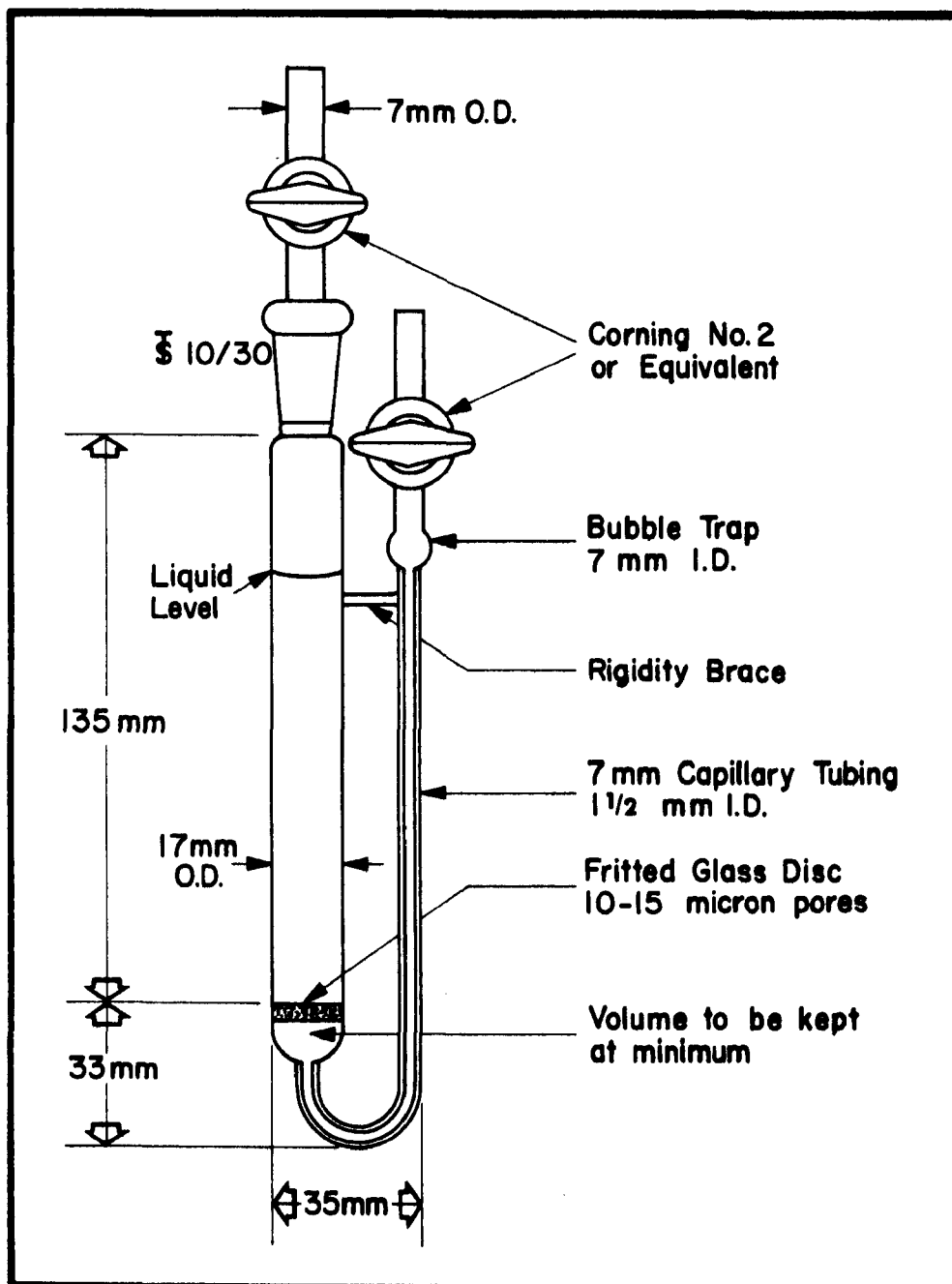


Figure 5
Emanation Tube (Bubbler)

DISSOLUTION OF SAMPLES FOR RADIUM-226 ANALYSIS

Principle of the Method:

Since individual samples are not constant in their composition, methods or variations of methods must sometimes be used for a complete digestion of the sample. The following methods for the dissolution of environmental samples were prepared in the hope of aiding in the more rapid final analysis of samples and to avoid the trial and error methods for the dissolution of different samples.

Reagents^{*}:

Hydrochloric acid, 3N
Hydrofluoric acid, 48%w
Hydrogen peroxide, 30%w
Sodium carbonate, C. P. grade granules
Sodium hydroxide, C. P. grade pellets
Nitric acid, 16N, 8N, 3N

Apparatus:

Analytical balance
Beakers, various
Dish, evaporating, #0
Filter paper, Whatman #42
Hotplate
Muffle furnace
Crucible, platinum, 30-ml
Burner, blast
Membrane filter and holder

^{*} See appendix A

Total Decomposition Methods:

See "Preparation of Samples for Strontium Analysis"

1. If the sample ash appears light in color or white ash with no visible carbon:
 - a) Transfer a weighed aliquot to a 400-ml beaker.
 - b) Digest with 100 ml 3N nitric acid.
 - c) Evaporate to near dryness, dissolve the precipitate with 3N nitric acid.
 - d) If the sample solution is clear with no visible precipitate, adjust the volume to 150 ml with distilled water and proceed, using suitable radium method. **
2. When the samples contain visible carbon or the samples have been digested in 3N nitric acid and show evidence of carbon:
 - a) Add 15 ml of 16N concentrated nitric acid.
 - b) Evaporate to near dryness.
 - c) Dilute the sample with concentrated nitric acid.
 - d) Add a few ml of 30% hydrogen peroxide.
 - e) Evaporate to near dryness and repeat steps c) and d), if necessary, until solution is clear.
 - f) If no visible precipitate remains, adjust volume to 150 ml with distilled water and proceed with suitable radium method. **
3. When obviously large amounts of carbon remain in the sample:
 - a) Transfer a weighed aliquot to a #0 Coors evaporating dish.
 - b) Wet the sample with 16N concentrated nitric acid.
 - c) Place the evaporating dish in a cold muffle furnace and slowly increase the temperature to 400°C. Repeat acid and heat if necessary.

** See "The Determination of Radium-226 in Environmental Samples by Radon Emanation."

- d) Cool, dissolve the ash with 8N nitric acid.
 - e) Transfer the sample to a 400-ml beaker using 3N nitric acid.
 - f) If no visible precipitate remains, adjust the volume to 150 ml with distilled water and proceed using a suitable radium method. **
4. When the sample has been dissolved in nitric acid and a visible residue remains:
- a) Filter the sample through a #42 Whatman filter paper.
 - b) Return the filtrate to the 400-ml beaker.
 - c) Transfer the filter paper with precipitate to a 30-ml platinum crucible.
 - d) Place platinum crucible in the muffle furnace until paper is ashed.
 - e) Cool, add a few mls of 48% hydrofluoric acid and take to dryness on the hot plate.
 - f) Repeat step e).
 - g) Dissolve the residue with 16N concentrated nitric, and take to dryness on the hot plate. Repeat.
 - h) Cool, dissolve the remaining residue with 3N nitric, swirl the platinum crucible to be sure of washing any remaining residue from the sides of the crucible.
 - i) Transfer the solution to original beaker, washing the platinum crucible with 3N nitric acid.
 - j) Adjust the volume of the sample to 150 ml with distilled water and proceed with suitable radium method. **

** See "The Determination of Radium-226 in Environmental Samples by Radon Emanation."

THE DETERMINATION OF RADIUM-226
IN WATER SAMPLES BY RADON EMANATION²

Principle of the Method:

An aliquot of the water sample is transferred to a 2-liter beaker. The radium is co-precipitated as a sulfate using a lead carrier. The lead-radium sulfate is re-precipitated as a carbonate. The carbonate precipitate is then dissolved in 3N nitric acid, transferred to a radon bubbler, and allowed to ingrow for 28 days.

Reagents^{*}:

Ammonium acetate, 6M
Lead nitrate carrier, 100 mg lead/ml
Nitric acid, 3N, 16N
Sodium carbonate, 3N
Sulphuric acid, 1N, 18N

Apparatus:

Hot plate, stirrer, magnetic, w/stir bars
pH meter
Tube, radon emanation (Fig. 5)

^{*}See appendix A

²D. E. Rushing, et al., "The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Radium, Polonium and Uranium," Rad. Hlth. & Safety in Mining and Milling of Nuclear Materials, Vol. II, 187 (1964), International AEC, Vienna, Austria.

Procedure:

1. Transfer a 1500-ml aliquot of the sample to a 2-liter beaker.
2. Adjust the pH to approximately 1.0 with concentrated nitric acid, add 10 ml lead carrier.
3. Heat to about 70°C with stirring on the magnetic stirrer hot plate.
4. Cautiously add 100 ml 18N sulfuric acid, continue stirring hot solution for a minimum of one hour.
5. Remove the sample from the stir plate and allow precipitate to settle overnight. Decant, discard the supernate and transfer the precipitate to a 40-ml centrifuge tube using 1N sulfuric acid.
6. Centrifuge, discard the supernate. Wash the precipitate with 10 ml of water, centrifuge, discard the supernate.
7. Rinse the walls of the 2-liter beaker with a few mls 6M ammonium acetate; transfer this solution to the precipitate in the centrifuge tube. Bring the volume in the centrifuge tube to about 25 ml with 6M ammonium acetate.
8. Heat in a water bath with stirring until the precipitate dissolves.
9. Slowly add 20 ml 3N sodium carbonate, heat and stir. Centrifuge, discard the supernate.
10. Dissolve the carbonate precipitate with 3N nitric acid, re-precipitate using 30 ml hot 3N sodium carbonate.
11. Heat for approximately 15 minutes, centrifuge, discard the supernate.

12. Dissolve the carbonate precipitate with 5 ml 3N nitric acid, transfer the sample to a radon bubbler (Fig. 5) with a maximum of 7 ml of distilled water.
13. Seal the bubbler and allow the sample to ingrow for 28 days before counting.

THE ANALYSIS OF RADIUM-226 IN SOIL

Principle of the Method:

This procedure describes a method for the determination of radium-226 in soil, sludge, air filters, feces, and urine ash. A suitable sample is transferred to a platinum crucible, mixed with Nicholson's flux and fused. The fused cake is dissolved in sulfuric acid and barium carrier is added. The barium sulfate is heated with phosphoric acid to form the soluble phosphate. The cooled barium phosphate is dissolved in hydrochloric acid and transferred to an emanation tube.

Reagents^{*}:

Ammonium sulfate, 10%w
Barium carrier, 10 mg/ml
Hydrochloric acid, 3N, 6N
Hydrofluoric acid, 48%w
Hydrogen peroxide, 3%w
Nicholson's flux
Phosphoric acid, concentrated
Sulfuric acid, concentrated, 0.5%

Apparatus:

Crucible, platinum, 30-ml
Emanation tube (Fig. 5)
Filter, membrane, Hawp 04700, 0.45 μ
Filter holder, membrane

^{*} See appendix A

Burner

Hot plate

Procedure:

1. Weigh a suitable sample into a 30-ml platinum crucible. Add 8 g Nicholson's flux, mix. (Notes 1, 2, and 3.)
2. Fuse over a burner until it is clear. (Note 4.)
3. Cool the crucible and place in a 250-ml beaker containing 120 ml distilled water. Add 20 ml concentrated sulfuric acid and 5 ml 3% hydrogen peroxide.
4. When melt has dissolved, rinse and save crucible for step 6. Add 10 ml barium carrier to precipitate barium sulfate and allow to stand overnight.
5. Filter through membrane filter and rinse beaker and filter several times with 0.5% sulfuric acid.
6. Transfer the filter and precipitate to the original platinum crucible. Dampen with 10% ammonium sulfate and add 0.5 ml concentrated hydrofluoric acid
7. Evaporate to dryness and ignite over blast furnace.
8. Cool and add 20 drops concentrated phosphoric acid.
9. Heat on hot plate at 200°C, then carefully heat over a burner with swirling until white fumes are no longer evolved.
10. Cool crucible and fill with 6N hydrochloric acid. Warm until free acid is removed.
11. Transfer the solution to an emanation tube with 3N hydrochloric acid and distilled water.
12. Seal and allow to ingrow for 28 days. (See "The Apparatus and Method for Radon Transfer" for de-emanation of radon.)

NOTES:

1. If organic matter is present, ignite overnight at 500°C.
2. Moisten air filter with 10% ammonium sulfate.
3. If more than a trace of heavy metals is present, a porcelain crucible should be used.
4. An occasional sample will require additional flux.

Calculation:

$$\text{pCi/l or g} = \frac{\text{cpm}}{F \text{ sample size (in liters or grams)}}$$

where: F is a factor that includes the counting efficiency and chemical efficiency of the method. It is determined by preparing similar type standards, i.e., adding a known amount of radium-226 to low-level bone ash, food ash, etc. After chemical separation of the radium and 30 days radon ingrowth, the standard is transferred and counted at the same time as the unknown.

$$F = \frac{\text{cpm of standard}}{\text{pCi of standard}}$$

THE DETERMINATION OF RADIUM-226 IN SOIL SAMPLES BY RADON EMANATION
(A Leach Method)

Principle of the Method:

A representative soil sample is leached with 3N hydrochloric acid, filtered and diluted to a known volume, which should be about 10 grams of soil leached to 10 ml of solution.

Ten ml of the solution are transferred to a radon bubbler and allowed to ingrow for a suitable length of time.

Reagents*:

Hydrochloric acid

Apparatus:

Motor stirrer with plastic impeller

Paper filter, Whatman #42

Procedure:

1. Transfer a weighed sample of soil to a suitable size beaker. Add approximately 20 ml 3N hydrochloric acid for each 10 grams of soil to be leached.
2. Heat on the hot plate and stir using an automatic stirrer for one hour.
3. Filter through a Whatman #42 filter paper using a Buchner funnel. Wash the residue with 3N hydrochloric acid.
4. Discard the residue and adjust the volume of the leach solution to approximately 10 ml of solution per 10 grams of soil leach.
5. Transfer 10 ml of the solution to a radon emanation tube and allow to ingrow for 28 days.

* See appendix A

DETERMINATION OF TRITIUM IN WATER

Principle of the Method:

A portion of the water sample is distilled to remove the water from any dissolved or suspended solids. Aliquots of the distillate are pipetted into counting vials together with a liquid scintillator solution. The sample is then counted in a liquid scintillation spectrometer. A standard tritium sample is counted for efficiency determination and a low-tritium water sample is counted for background.

Reagents*:

Liquid scintillation solution³

Tritium standard, National Bureau of Standards

Apparatus:

Pipet, 5-ml, 20-ml

Spectrometer, liquid scintillation

Vial, polyethylene, screw cap, 25-ml

Procedure:

1. Distill a 10-50 ml portion of the water sample just to dryness. The first steam is vented, and the distillate collected in a cold trap.
2. Pipet a 5-ml portion of the distillate into the polyethylene counting vial (Note 2) together with 20 ml of the liquid scintillator solution.

*See appendix A

³A. A. Moghissi, H. L. Kelley, J. E. Regnier and M. W. Carter, "Low-Level Counting by Liquid Scintillation--I. Tritium Measurement in Homogeneous Systems," *Intn'l. J. of Applied Rad. & Isotopes*, Vol. 20, pp. 145-156, (1969), Pergamon Press.

3. Make a background sample by pipetting a 5-ml portion of low-tritium water (Note 3) into a vial containing 20 ml of liquid scintillation solution.
4. Make a standard sample by pipetting a 5-ml portion of a diluted National Bureau of Standards standard into a vial containing 20 ml of liquid scintillation solution.
5. Place the unknown, background, and standard samples in the liquid scintillation spectrometer and, after the solutions have dark-adapted, usually about 5 hours, count for 100 minutes each. (Note 4.)
6. The sample counting data are corrected for background and efficiency and the picocuries of tritium per liter of sample are calculated.

Calculation:

$$T = \frac{D (C-B) (1000)}{2.22 \times S \times 5}$$

where T = pCi tritium per liter of water

D = dpm tritium in standard vial

C = cpm in the sample vial

B = average background in cpm

S = average cpm in the standard vials

2.22 = dpm/pCi

1000 = ml/l

5 = ml H₂O in sample

The standard deviation reported is that obtained from counting statistics.

NOTES:

1. Vacuum distillation removes the water from dissolved solids which may be a source of contamination or could cause further quenching of the liquid scintillation process. (A thermal distillation may be used in place of vacuum.)
2. The polyethylene vials are used because they provide a higher counting efficiency and lower background than those made of glass.
3. The low-tritium water used was obtained by distilling fossil water removed from an oil well.
4. The standard sample may be used to set correctly the upper and lower discriminators of the spectrometer.

RADON IN ATMOSPHERIC SAMPLES

Principle of the Method:

This method describes a procedure for the separation and collection of radon from atmospheric samples. The samples as received are of two types: a "grab" sample of 1 or 2 liters and an integrated sample representing 48 hours of sampling. All of the "grab" sample or a portion of the integrated sample is transferred to the gas separation apparatus. The sample is then passed through carbon dioxide and water removal trap, and, then, through two charcoal traps at ice water temperature. The radon is de-emanated with helium and collected in scintillation cells.

Reagents :

Ascarite
Charcoal
Drierite

Apparatus:

See Fig. 6
T₁ - steel ball trap
D₁ - Ascarite & Drierite
C₁ - Charcoal
C₂ - Charcoal

Procedure:

1. Attach sample container to the sample-in line (see Fig. 6) and evacuate all lines and bulb A. Record pressure and temperature.

2. Transfer all of the "grab" sample into bulb A, or bring bulb A to atmospheric pressure with the integrated sample. Record pressure and temperature.
3. With T_1 in ice water, D_1 in dry ice-acetone (DIA), C_1 and C_2 in ice water, establish flow: bulb A - T_1 - D_1 - C_1 - C_2 - vacuum.
4. Continue flow until pressure in bulb A returns to original pressure (approximately 10 minutes).
5. Close all stopcocks and turn off vacuum pump. Remove ice water from C_1 and replace with a furnace preheated to 400°C .
6. Establish flow C_1 - peristaltic pump - first scintillation cell. Pump for 1 minute.
7. Turn off pump, open helium valve and allow helium to mix in C_1 for one minute. Repeat step 6.
8. Repeat transfer procedure step 7 six times.
9. Establish flow C_2 - peristaltic pump - second scintillation cell - remove ice water and replace with 400°C furnace. Pump for one minute.
10. Repeat step 7 and 8 six times.

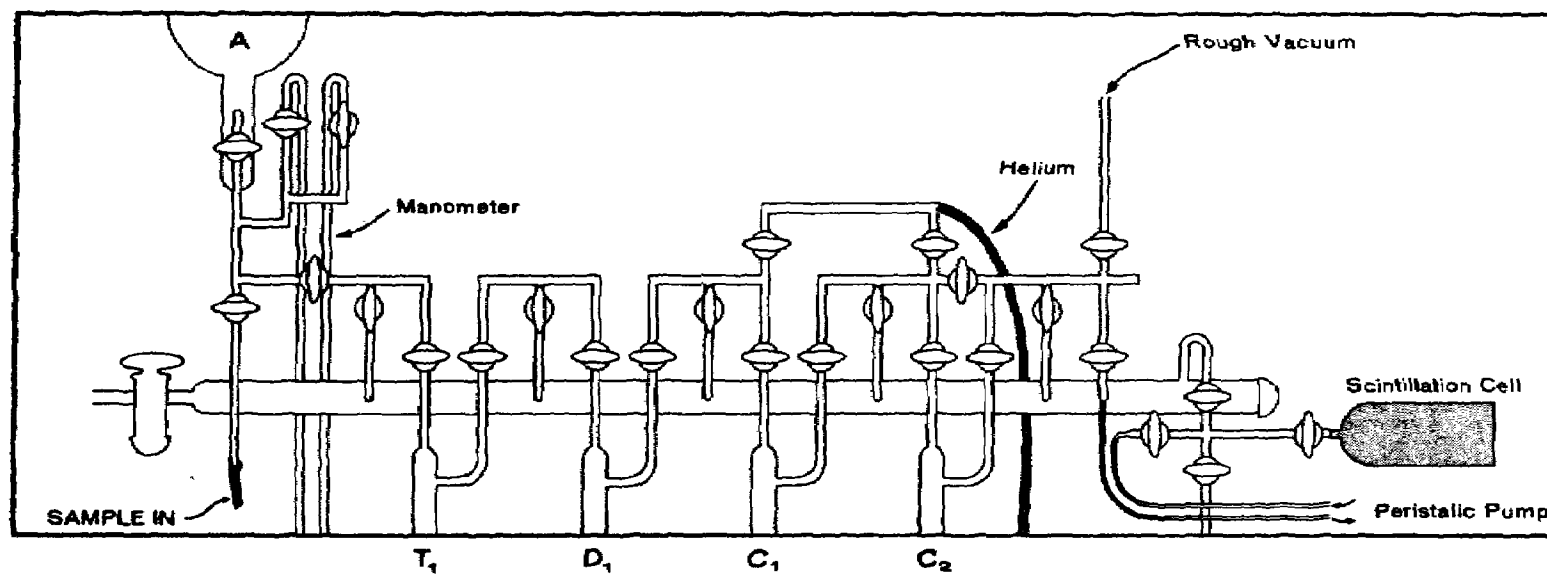


Figure 6
Apparatus for Radon in Air

A PROCEDURE FOR THE SEPARATION OF RADIOKRYPTON
RADIOXENON, (RADON-222), WATER, AND CARBON DIOXIDE
IN ATMOSPHERIC SAMPLES⁴

Principle of the Method:

This method describes a procedure for the separation of various gaseous radionuclides from gross air samples. The air samples are received either as a "grab" sample, or a "cryogenic" sample. The grab sample represents approximately 10 cubic feet of air collected at a flow of 10-15 cubic feet per minute. The cryogenic sample represents an integrated sample collected at a flow of 3-4 cubic feet per minute. The sample is transferred to the gas analysis apparatus. Water is removed by freezing and distillation. The radiokrypton, radioxenon, radon-222, and carbon dioxide are separated by elution through a molecular sieve column at various temperatures. The volumes of the separated gases are measured for yield determination and transferred to appropriate counting chambers.

Reagents^{*}:

Hyamine-methyl alcohol
Charcoal, 16-20 mesh
Molecular sieve 5A, 30-60 mesh
Liquid nitrogen
Dry ice
Acetone
Helium
Water baths, 0°C and 100°C
Xenon carrier
Krypton carrier

^{*}See appendix A

⁴F. F. Momyer, "The Radiochemistry of the Rare Gases,"
National Academy of Sciences, Nuclear Science Series.

Apparatus:

Gas analysis apparatus (Fig. 7)

Description of Apparatus:

A standard vacuum arrangement consisting of a mechanical fore pump, an oil diffusion pump and a trap refrigerated in liquid nitrogen is used to obtain a base pressure of 10⁻⁶ mm helium. This system is protected by a vacuum controller which will shut down the system if leaks occur. From left to right in Fig. 7 the various components of the apparatus are:

T_w - water trap

T₁ - 40 mm ID Trap packed with 3/16" stainless steel balls and glass wool

P₁ - differential manometer (not illustrated)

C₁ and C₂ - 40 mm ID Trap packed with 100 gms of 40-60 mesh activated charcoal

M₁ and M₂ - six feet of 12 mm ID tubing packed with 30-60 mesh molecular sieve 5A

T₂ - 20 mm ID Trap packed with 1/8" steel balls

C₃ - 20 mm ID Trap packed with 15 g activated charcoal

T₃ - 20 mm ID Trap - empty

A - measuring system calibrated to 0.1 ml

B - 100-ml bulb calibrated to 0.1 ml

C - 1000-ml bulb calibrated to 1 ml

It is not possible to show on the line-drawing all of the valving and vacuum connections necessary for the operation. However, a purified helium supply is provided at the inlet to all traps. The outlet of all traps except T₁ have connection to an ionization chamber and thermal conductivity cell (ICTC system). The ionization chamber current is amplified with a vibrating reed electrometer whose output drives one

pen on a 2-pen recorder. The thermal conductivity cell unbalances a whetstone bridge circuit which in turn drives the second pen of the recorder. A continuous record of the location of the activity, or added carrier, is thus maintained throughout the separation. Various other pieces of hardware are necessary to effect the separation: 400-500 watt portable induction heater, electric furnaces capable of attaining 350°C in a short time, temperature indicator (0-400°C), 500-watt immersion heater, several 1-liter and 500-ml Dewar flasks, and adjustable transformer.

Procedure:

I. Initial Preparation

All traps are degassed at 350°C and evacuated until a pressure of 10^{-4} mm is obtained. Carriers of stable xenon and krypton are prepared by measuring the volume, pressure, and temperature in the calibrated section (A and B, Fig. 7), and placed on the sample in line.

The ionization chamber and thermal conductivity cell are zeroed with a flow of helium.

T₁ and C₁ are cooled with liquid nitrogen (LN).

II. Sample Transfer

Because of the difference in sampling technique, the transfer of the sample will be treated separately:

A. Grab

The weight and pressure of sample bottle are recorded. The bottle is connected to the sample inlet port and placed in a heating mantle. Using a roughing vacuum pump on exit from C₁ and suitable valving, establish sample flow through T₁ and C₁ of about 15 liters per minute and 35 cm pressure. (Reduced pressure is necessary to avoid condensation of liquid air in system.) Continue bleeding

sample into T_1 and C_1 until the pressure drops to less than 10 cm helium. Shut off sampling inlet port and add the carriers. Record transfer time (about 20-30 minutes).

B. Cryogenic:

Remove the sampler from the LN Dewar and place in a furnace capable of reaching 350°C in 45 minutes, attach helium line to inlet of sampler and outlet to sample inlet port. After checking for leaks, with suitable valving use needle valve on helium to establish flow through T_1 and C_1 of 15-20 liters/minute at 35 cm helium pressure with roughing pump. Continue adding sample until the molecular sieve container is at 350°C , hold for 30 minutes, shut helium valve and sample port, and add carriers. Record transfer time (from 1 1/2 to 2 hours). At this point, T_1 contains water, carbon dioxide, xenon, and krypton; C_1 contains carbon dioxide, krypton, xenon, oxygen, and nitrogen.

III. Water Removal and Recovery:

1. Isolate C_1 from T_1 by closing stopcock. T_1 is heated with induction heater until the pressure as indicated on P_1 is constant.
2. Dry ice acetone slush is then placed around T_1 and allowed to remain until the water is frozen and pressure on P_1 is again constant.
3. Any gases are then transferred to C_1 by adsorption on charcoal. Repeat these steps to assure that no gases are dissolved in water.
4. Transfer water to water trap by heat on T_1 and LN on water trap until all water is removed (about 1 hour). Transfer lines might need to be warmed gently to affect complete transfer. Submit for tritium analysis. (See "Determination of Tritium in Water.")

IV. Air Removal from C₁:

5. With C₁ in LN, establish helium flow (600-800 ml/min) through the C₁ ionization chamber thermal conductivity cell (ICTC) vent. Remove LN from C₁ and replace with dry ice acetone (DIA) slush. Continue this flow until all of the air is removed as evidenced by a return of the TC pen recorder to the base line (approximately 55 minutes). Shut vent valve and helium flow.

V. Removal of Krypton, Xenon, and Carbon Dioxide (Radon) from C₁:

6. Leave DIA on C₁ and re-establish helium flow C₁-ICTC-M₁-vent. M₁ is in LN when flow is stabilized. Remove DIA from C₁ and replace with electric furnace and start heating. (A sharp increase on the ICTC is noticed almost immediately but drops off in a short time. This is due to residue air and a change of temperature in the ICTC system.)
7. Continue heating until a temperature of 350°C is reached and all of the carriers and carbon dioxide are transferred. This is indicated by a return to base line by the TC (a shift in base line is usually noted at this point due to the higher temperature of the gases entering the ICTC and also a decrease in flow rate).
8. Shut vent and turn off helium flow. Open high vacuum valve to C₁ and continue heating until a temperature of 350°C is reached and a vacuum of less than 10⁻⁴ mm helium is obtained. (C₁ is then ready for another run.)

VI. Separation of Krypton, Xenon, and Carbon Dioxide from M₁:

9. With LN on M₁ and C₂, establish helium (200-300 ml/min) M₁-ICTC-C₂-vent.

10. Remove LN from M_1 and replace with ice water slurry. After approximately ten minutes, a sharp increase in the ICTC is noted. This is the krypton. Continue helium flow until the TC returns to base line (8-10 minutes).
11. Rearrange helium flow, M_1 -ICTC- T_3 in LN-vent.
12. Replace ice water with hot water (90° - 100° C). The xenon appears on the ICTC in approximately five minutes. Continue flow and heating until the TC returns to base line. Some alpha pulses will be noted on the TC at this time indicating radon. Radon may either be vented (bypassing T_3) or collected in a separate charcoal-packed trap with LN.
13. Rearrange helium flow, M_1 -ICTC- T_2 in LN-vent.
14. Remove boiling water and replace with electric furnace. Continue flow, raising temperature to 350° C, until the TC returns to base line.

VII. Removal of Xenon:

15. The helium gas is purged from T_3 in LN by rapidly opening and closing the vacuum valve. Bulb B is cooled with LN and flow established from T_3 to B.
16. LN removed from T_3 and hot water applied. The xenon is thus distilled to bulb B. When all of the xenon is transferred, as evidenced by a constant reading on the manometer, close valve a, Fig. 7.
17. Remove LN from bulb and allow the xenon to vaporize. When pressure reading has stabilized, record pressure and temperature. Place LN on tip D and solidify the xenon. Close valve c and d, Fig. 7. Open valve b and f to counting chamber and system. (Care must be taken as a pressure above atmospheric is obtained at this point.)

18. Close valve f and place LN on bulb B, open valve c and again freeze out the xenon. Close valve b, open valve d, and allow xenon to reach temperature equilibrium. Record pressure and temperature. (First reading minus second reading equals amount of gas transfer to counting chamber and counted.)

VIII. Removal of Krypton:

19. With LN on C₂ and T₃, set up flow C₂-T₃, flash off the helium from C₂ by rapidly opening and closing vacuum valve. Remove LN from C₂ and replace with electric furnace. Continue heating until a temperature of 300°C is reached.
20. After all the krypton is in T₃, continue as in "VII. Removal of Xenon." A difference of 2-3 mm will always be noted on manometer. (Vapor pressure krypton at LN temperature.)

IX. Removal of Carbon Dioxide:

21. With LN on T₂ and T₃, set up flow T₃-ICTC-T₃-vent. Remove LN from T₂ and replace with warm water. Continue transfer until TC returns to base line. Shut helium flow and vent. Flash helium from T₃. A gas tube with frozen hyamine-methyl alcohol is placed at counting tube outlet.
22. Transfer to measuring system as in xenon-krypton removal. Close valve a, and remove LN from B as carbon dioxide sublimes. Carefully observe pressure rise. If pressure goes over 1 atm., open valve g, Fig. 7. When gas has come to equilibrium, record pressure and temperature.
23. Valve g is closed, valve b and f are opened, and the carbon dioxide in A and B is transferred to gas tube.
24. The excess carbon dioxide in bulb C is then transferred to a gas bulb and vented to atmosphere. Excess pressure is to be avoided.

Calculations:

V_A = volume of bulb A, ml

V_B = volume of bulb B, ml

P_1 = pressure of carrier, mm

T_1 = temperature of carrier, °K

V_1 = volume of carrier, ml

$$V_1 = (V_A + V_B) \frac{(P_1)}{(760)} \frac{(273)}{(T_1)}$$

and P_2 = pressure of carrier after separation, mm

T_2 = temperature of carrier after separation, °K

V_2 = volume of carrier after separation, ml

$$\% \text{ recovery of carrier} = \frac{V_2}{V_1} \cdot 100$$

P_3 = pressure of carrier of transfer to counting tube, mm

T_3 = temperature of carrier of transfer to counting tube, °K

V_3 = volume of carrier of transfer to counting tube, ml

$$V_3 = (V_A + V_B) \frac{(P_3)}{(760)} \frac{(273)}{(T_3)}$$

$$\% \text{ carrier in counting tube} = \frac{V_2 - V_3}{V_2} \cdot 100$$

for xenon:

$$\text{pCi/total sample} = \frac{\text{cpm}}{2.22 \text{ CE } (\% \text{ recovery})(\% \text{ sample in counting tube})}$$

where CE = counting efficiency

$$\text{cpm} = \frac{\text{gross counts} + \text{instrument background}}{\text{counting time}}$$

for krypton:

pCi/total sample =

$$\frac{1}{2.22 (\% \text{ recovery}) (\% \text{ sample})} \times \frac{\text{cpm}}{\text{CE}} = \text{dpm/ml} \cdot \text{ml in counting chamber}$$

where dpm/ml = krypton-85 activity in carrier gas

carbon dioxide:

$$V_{\text{CO}_2} = V_A + V_B + (V_C) \cdot \frac{P_4}{760} \cdot \frac{273}{T_4}$$

where P_4 = pressure of carbon dioxide in either V_A , V_B , or V_C

where T_4 = temperature of carbon dioxide in either V_A , V_B , or V_C

The volume of carbon dioxide used for carbon-14 analysis is the volume of gas in Volume A + B. (See "Determination of Carbon-14" for further calculation.)

tritium:

Weight of water recovered x pCi tritium/g = pCi tritium total sample.

Miscellaneous Data:

Density of air = 1.29299/liter

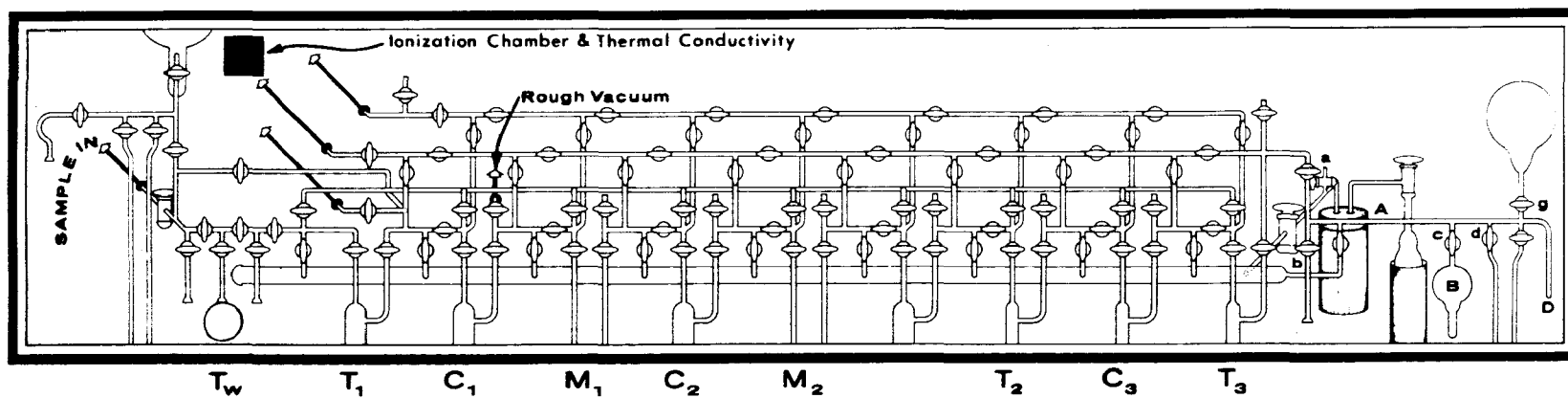


Figure 7
Apparatus for Xenon and Krypton in Air

WATER AND CARBON DIOXIDE RECOVERY FROM MOLECULAR SIEVE

Principle of the Method:

Molecular sieve which has been exposed to moisture and carbon dioxide in the atmosphere is transferred to a cannister. The water and carbon dioxide are removed by the use of heat and a carrier gas. A modification of the method is required if hydrocarbons are present.

Reagents^{*}:

Molecular sieve-13X-1/16" pellets

Apparatus:

Photograph #1 shows the two molecular sieve samplers used at SWRHL and the cannister for degassing.

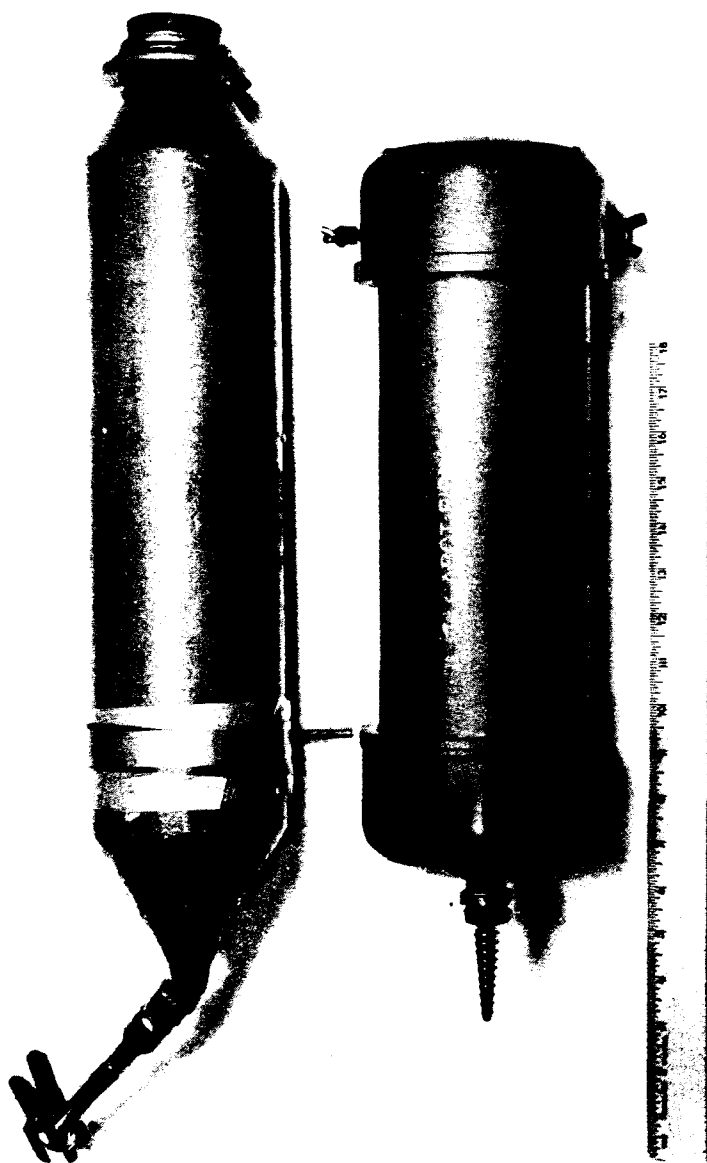
Procedure:

1. Transfer sample rapidly from sampler to cannister, seal, and pressurize with helium.
2. After checking cannister for leaks, place in heater.
3. Set up flow helium-cannister-sample in-T₁ (LN)-C₁ (LN)-rough pump.
4. Bring temperature of cannister to 400°C and hold. Heat sample inlet line to remove condensed water. If hydrocarbons are present, proceed as in steps (a) through (d) below:
 - (a) With helium valve closed, close sample inlet valve.

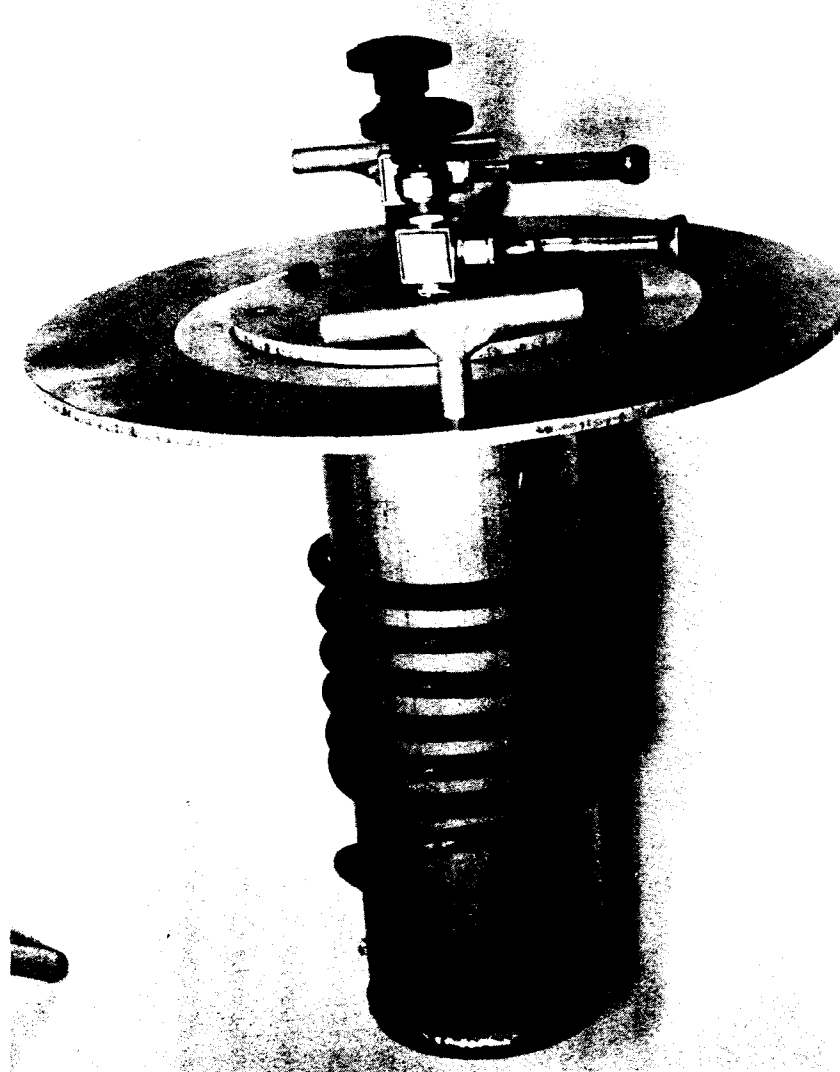
^{*} See appendix A

- (b) Close all stopcocks except pressure gauge.
 - (c) Remove LN from T_1 . Replace with heater. When all ice is melted, replace heater with DIA and refreeze.
 - (d) Open stopcock to C_1 and transfer any carbon dioxide or air to C_1 . Close stopcock. Hold temperature of cannister at 400°C . Replace LN on T_1 , set up flow, helium-cannister- T_1 - C_1 -pump. Continue with steps 6 through 15.
5. When visible water is no longer noticeable in glass transfer line, close helium line, continue rough pump until lowest pressure on manometer is reached. Close sample inlet valve and re-pressurize cannister with helium. (MS is now ready for re-use.)
 6. Close all stopcocks except pressure gauge.
 7. Remove liquid nitrogen from T_1 . Replace with heater. When all ice is melted, replace heater with DIA and refreeze.
 8. Open stopcock to C_1 and transfer any carbon dioxide or air to C_1 . Close stopcock.
 9. Distill water from T_1 to W_1 , W_2 , or W_3 by setting up flow T_1 to W_1 , W_2 , or W_3 . Remove DIA and replace with heat.
 10. To remove air from C_1 set up flow helium- C_1 (LN)-ICTC-vent. Remove LN from C_1 . Replace with DIA, continue helium flow until recorder pen on ICTC returns to base line.
 11. Transfer carbon dioxide and any other gases to MS_1 by setting flow, helium- C_1 (DIA)-ICTC- MS_1 (LN)-vent. Replace DIA with 350°C heater and continue flow until all gases are transferred.
 12. Set up flow, helium- MS_1 (LN)-ICTC-vent. Remove LN and replace with 100°C water to remove any xenon or krypton.
 13. Set up flow, helium- MS_1 (100)-ICTC- T_3 -vent. Remove 100° water, replace with heater and continue flow at 350°C until all carbon dioxide is transferred.

14. Proceed as in section IX. of, "A Procedure for the Separation of Radiokrypton, Radioxenon, (Radon-222), Water, and Carbon Dioxide in Atmospheric Samples." If water only is required, gaseous nitrogen may be used as a carrier gas with DIA on T₁ instead of LN.



Molecular Sieve Samplers



Degassing Cannister

RADON IN NATURAL GAS

Principle of the Method:

Methods are described for the analysis of radon-222 in natural gas. The first method is a direct transfer of the natural gas to Lucas scintillation detectors for samples that are 1 to 2 half-lives old. The second method describes a procedure for the concentration of radon in any type of natural gas sample (crude or processed).

In the direct transfer method the sample is transferred directly to the Lucas detectors with water and carbon dioxide removed. In the concentration step, a large sample is passed through a room temperature molecular sieve to remove heavy boilers (C_5 , and higher), a steel ball trap at liquid nitrogen temperature (to collect C_2 - C_5 's), and a charcoal trap at liquid nitrogen temperature (to collect methane, radon and any other low boilers). Any methane or radon collected in the steel ball trap is transferred to the charcoal trap by warming to dry ice-acetone temperatures. Methane is removed from the charcoal trap by elution with helium. The radon is transferred into two smaller charcoal traps by elution and heat. The radon in each of the small traps is transferred to the scintillation cells.

Apparatus:

Same vacuum system as in the xenon-krypton method except for location of traps. (See Fig. 7)

Method A - Direct Transfer (See Fig. 8):

1. Attach sample bottle to sample in with an Ascarite-Drierite drying tube in line.
2. Evacuate all transfer lines and scintillation cells. Close vacuum valve and check for leaks. (A movement of mercury in manometer will indicate a leak.)

3. When transfer system is leak-free, gradually open regulator valve and transfer sample to three scintillation cells.
4. When pressure in the cells reaches atmospheric pressure (as indicated on the manometer), close all valves and record pressure and temperature.
5. Remove scintillation cells for alpha counting.

Method B (Refer to Fig. 9 for symbols):

1. Attach gas sample bottle with regulator to the sample-in line. Evacuate all lines and bulb I. Open regulator valve and allow sample to enter bulb I. When pressure, as noted on manometer II, reaches atmospheric shut regulator valve and record pressure and temperature of bulb I.
2. Close valve III and evacuate all lines to remove excess sample.
3. With M_1 at room temperature, T_1 and C_1 at liquid nitrogen temperature, set up flow, sample- M_1 - T_1 - C_1 . The adsorption of the sample on charcoal at liquid nitrogen temperature will cause the complete transfer of the sample to the three traps as indicated by the manometer.
4. Set up flow, Helium- M_1 - T_1 - C_1 -vent. Place warm water approximately 60°C on M_1 and allow to flow for 10 minutes. This will transfer any adsorbed methane and radon to the steel ball trap and charcoal and retain the C_5 's or higher hydrocarbons.
5. Close all stopcocks. Remove liquid nitrogen from T_1 and replace DIA. When T_1 has warmed to DIA temperature as indicated on differential manometer P_1 , open stopcocks between T_1 and C_1 to allow all gases with a boiling point below DIA temperature to transfer to C_1 .

6. Set up flow (600-800 ml/min.), helium-C₁-vent. Remove liquid nitrogen from C₁ and replace with DIA to remove methane and any oxygen or nitrogen.
7. When methane is removed, about 40 minutes, with DIA on C₁, C₂ and C₃, set up flow, helium-C₁-C₂-C₃-vent. Remove DIA from C₁ and replace with a 350°C heater.
8. When all of the sample has been transferred to C₂ and C₃, close helium and vent valve. Set up flow, C₁-C₂-C₃-vacuum to remove all of the helium from traps and insure transfer of all the sample to C₂-C₃.
9. With Lucas scintillation cell evacuated, set up flow C₂-pump-cell. Turn pump speed control to 40 (about 30 ml/min), this will insure that the sample being transferred will not blow a stopcock if pressure build-up is too rapid. Remove DIA and replace with 400°C heater. When trap temperature reaches 400°C, turn off pump and stopcocks, fill trap with helium and allow to set for three minutes (timed), then pump to scintillation cell for 5 minutes. Close stopcocks, shut off pumps and remove scintillation cell for alpha counting.
10. With all stopcocks closed, set up flow, C₃-pump-cell. Replace on C₃ with 400°C heater and fill C₃ with helium. When temperature reaches 400°C in trap, pump sample to scintillation cell. Repeat four times.
11. Remove scintillation cells for alpha counting.
12. Apply vacuum to all traps in preparation for next determination.

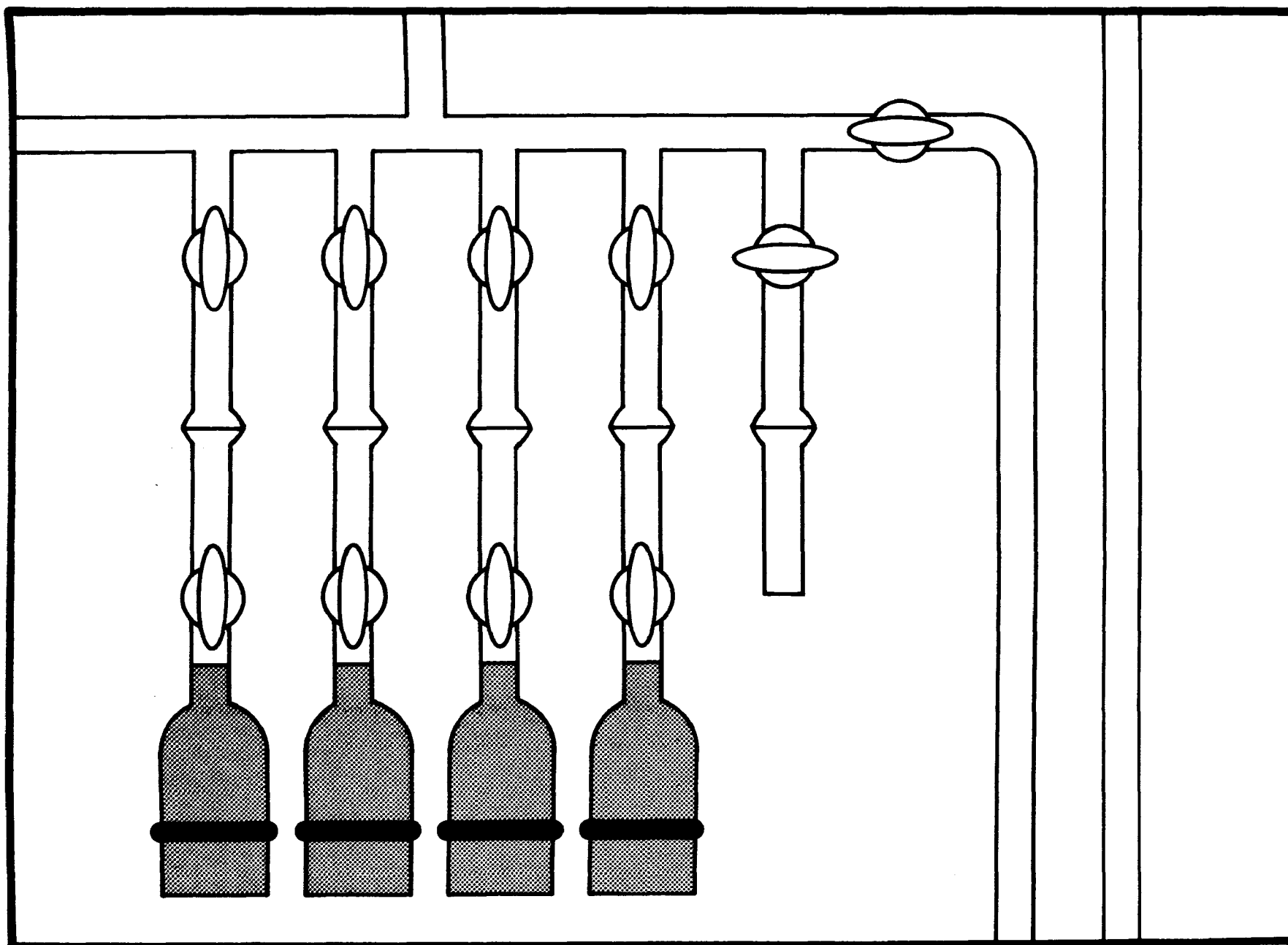


Figure 8
Radon in Natural Gas - Direct Transfer

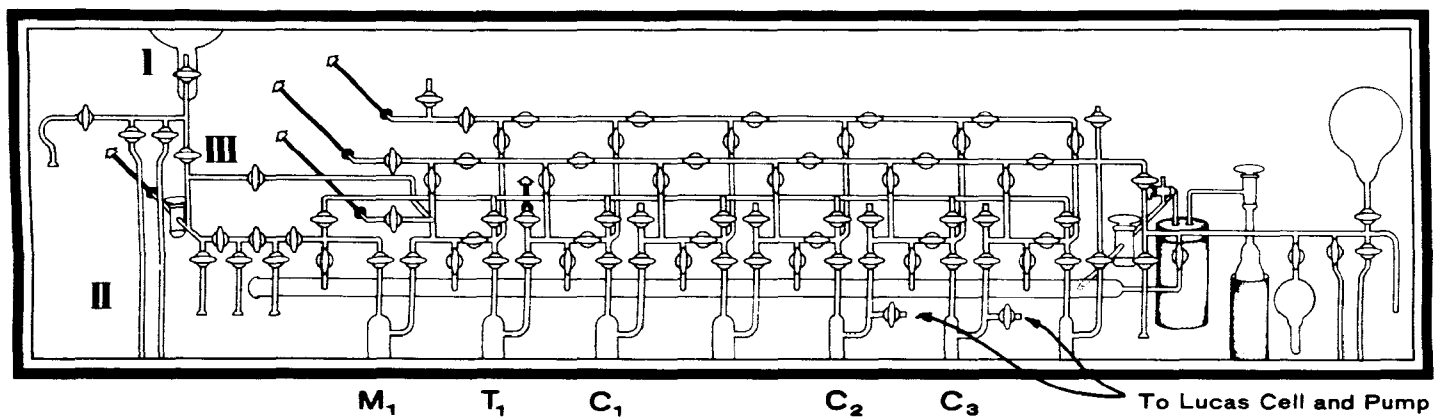


Figure 9
Radon in Natural Gas - Concentration Method

PREPARATION OF NATURAL GAS SAMPLES FOR ANALYSIS

Principle of the Method:

This method describes a procedure for the combustion of the hydrocarbons and the subsequent separation of water and carbon dioxide. This method is further used for the preparation of gas samples for radioxenon and/or radiokrypton analysis.

Apparatus:

Combustion apparatus (Photograph 2)

Procedure:

1. Evacuate the complete system to remove air and to check for leaks. Record room temperature and pressure (T_1 and P_1).
2. With control valve B and vacuum valve V closed, carefully open sample-in valve A until a reading of approximately twice atmosphere is noted on open tube manometer. Close valve A and record temperature and pressure reading on manometer (T_2 and P_2).
3. Set up an oxygen flow of 300 ml/min. on the flowmeter through the burner, both water traps (T_1 and T_2) and charcoal trap C and then to vent, all in DIA.
4. Apply high voltage by Tesla coil to sparker in burner and carefully open valve C. When ignition occurs, remove Tesla coil and adjust flame to 1/4" of bright blue flame.
5. Continue combustion until the pressure decreases to approximately atmospheric as indicated by a small differential on open tube manometer. Close valve C and record final pressure on open tube manometer (P_3 and T_3).
6. Close oxygen valve D. P_3 , valve E, and vent valve G. See water recovery section below.

7. Transfer C_1 to gas analysis apparatus as illustrated on Photograph 2.
8. Set up flow $He-C_1$ (DIA)- T_3 (LN)-vent. Remove DIA and replace with heater. Heat to $350^{\circ}C$ to distill all of the carbon dioxide into the steel ball trap. Flush helium from T_1 and proceed as in section IX, No. 21, of "A Procedure for the Separation of Radio-krypton, Radioxenon, (Radon-222), Water, and Carbon Dioxide in Atmospheric Samples."
9. Remove DIA from T_2 and replace with heater. Distill the water in T_2 into T_1 (still at DIA temperature).
10. Remove T_1 and allow to warm to room temperature, weigh and record weight of water recovered and submit for tritium analysis.

For radioxenon and radiokrypton, the only changes are C_1 is at LN temperature and the combustion is repeated three times.

Calculation:

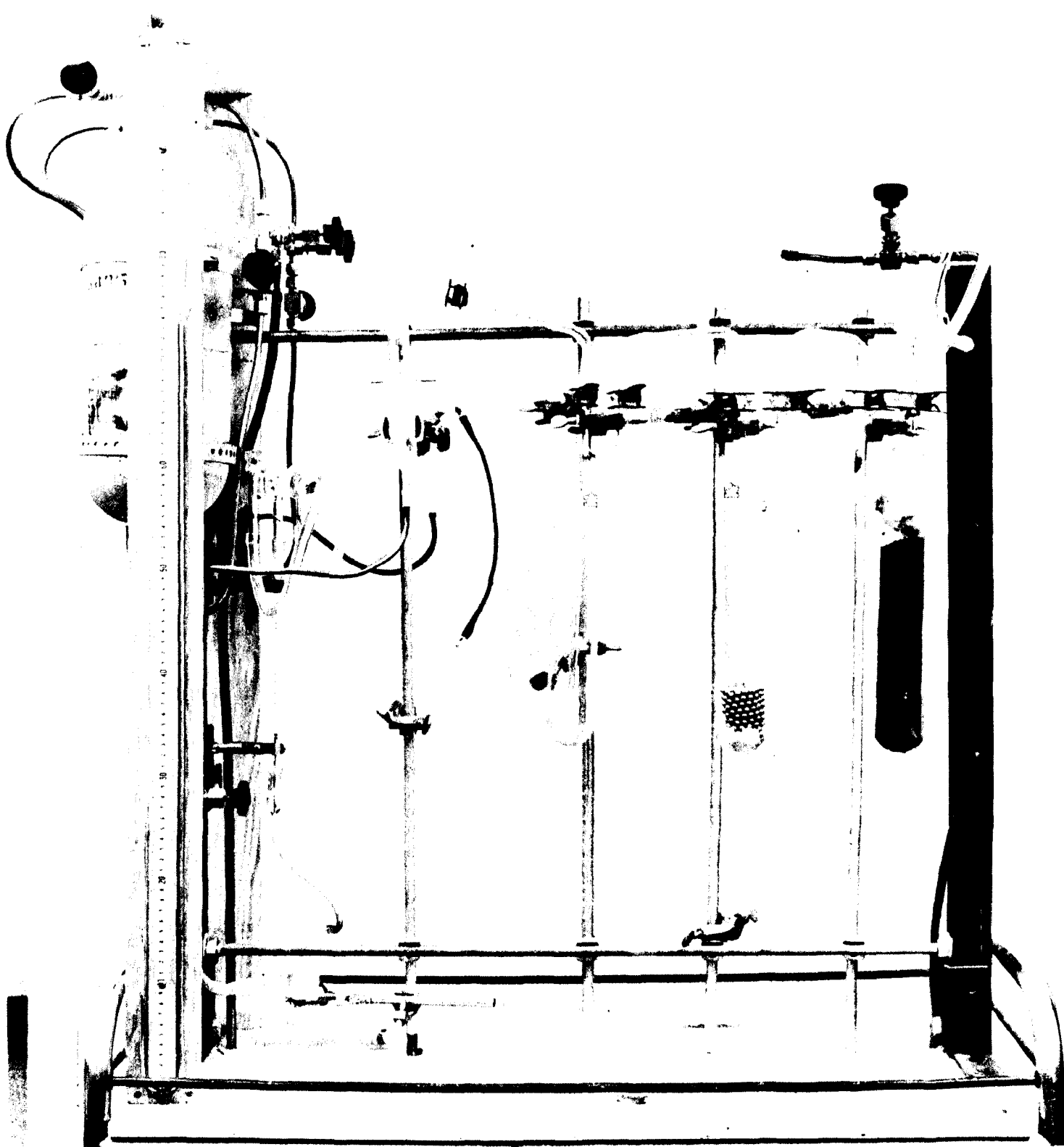
$$\frac{V_1(P_2 + P_1) 273}{760 (T_1)} = V_2$$

$$\frac{V_1(P_3 + P_1) 273}{760 (T_1)} = V_3$$

$$V_2 - V_3 = \text{ml of sample used at standard condition}$$

$$\text{pCi } ^3\text{H/cu. ft.} = \frac{28,300 \text{ ml} \cdot \text{pCi } ^3\text{H/ml of recovered H}_2\text{O} \cdot \text{ml recovered H}_2\text{O}}{\text{ml gas sample}}$$

$$\text{pCi } ^{14}\text{C/cu.ft.} = \frac{28,300 \text{ ml} \cdot \text{pCi } ^{14}\text{C/ml of recovered CO}_2 \cdot \text{ml recovered CO}_2}{\text{ml gas sample}}$$



Photograph 2
Combustion Apparatus

A PROCEDURE FOR THE SEPARATION OF RADIOXENON AND RADIOKRYPTON
FROM NATURAL GAS

Principle of the Method:

The method describes a procedure for the separation of radioxenon and krypton in natural gas. After the sample has been converted to carbon dioxide and water, and the water separated by freezing, the gases are adsorbed on charcoal at liquid nitrogen (LN) temperature and separated from carbon dioxide and each other by a series of low temperature chromatographic steps.

Apparatus:

Same as in Fig. 9.

See Fig. 10 for location of traps and columns.

From left to right the various components are:

- CS - charcoal trap containing carbon dioxide, xenon,
and krypton
- MS₁ - 250-ml molecular sieve, 13X
- C₁ - charcoal trap
- MS₂ - 250-ml molecular sieve, 13X
- MS₃ - molecular sieve, 5A
- C₂ - charcoal trap
- T₁ - empty trap

Procedure (See "Preparation of Natural Gas Samples for Analysis."):

1. IN A HOOD remove liquid oxygen (LOX) by establishing a helium flow through trap CS at LN temperature.
2. After LOX has been removed, transfer the trap and sample to the gas apparatus.

3. Establish flow to vent and by lowering the LN trap and warming with the palm of the hand, remove remaining LOX.
4. Set up flow, CS(LN)-MS₁-C₁(LN)-rough pump and add carrier xenon and krypton. Shut off rough pump.
5. Set up flow, helium-sample trap (LN)-ICTC-MS₁ (room temperature)-C₁(LN)-vent. Remove LN from sample trap, replace with a cold heater. Very slowly increase temperature to 350°C.
6. Set up flow, helium-C₁(LN)-ICTC-vent. Remove LN from C₁, and replace with DIA. Continue helium flow until all of the air is removed as indicated by a return to base line on the TC recorder.
7. Evacuate sample trays with vacuum. Place 350°C heater on MS₁ and evacuate with rough pump to remove carbon dioxide. Allow MS₁ to return to room temperature.
8. Set up flow, helium-C₁(DIA)-MS₁(room temperature)-ICTC-MS₂(room temperature)-MS₃(LN)-vent. Remove DIA from C₁ and replace with 350°C heater.
9. After all of the sample has been transferred to MS₃ as indicated by return to base line of ICTC recorder, set up flow, helium-MS₃(LN)-ICTC-vent (nearest C₂) 0°C. Allow just one minute flow to vent, then rearrange flow through C₂ vent.
10. After krypton removal is complete as indicated by a return to base line on ICTC recorder, set up flow, helium-MS₃0° (water)-ICTC-T₁-vent. Remove 0° water from MS₃ and replace with boiling water.
11. After xenon removal, proceed as in step VII, No. 15, "A Procedure for the Separation of Radiokrypton, Radioxenon, (Radon-222), Water and Carbon Dioxide in Atmospheric Samples."

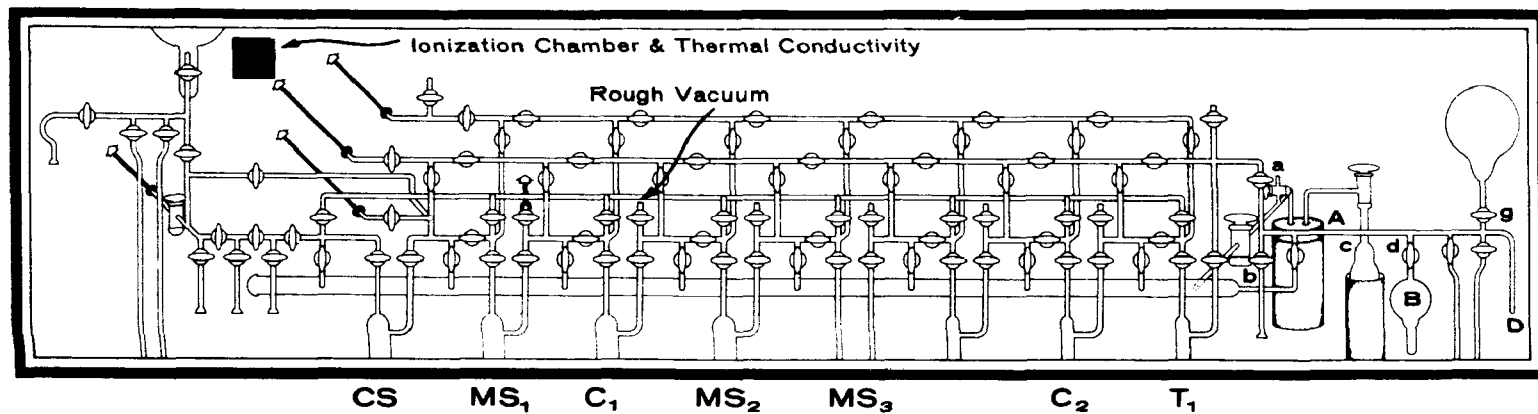


Figure 10
Apparatus for Separation of Xenon and Krypton
in Natural Gas

ANALYSIS OF URANIUM BY FLUOROMETRY

Principle of the Method:

This procedure describes a method for the determination of uranium in environmental samples. After dissolution of the sample, a uranium-uranium fluoride complex is formed that will fluoresce under ultra-violet light, unlike the contaminants. This method combines the advantages of several existing methods to reduce "inherent errors," operation error, and procedural tedium,

Reagents ^{*}:

Aluminum nitrate
Ammonium hydroxide, concentrated
Hydrofluoric acid, concentrated
Methyl isobutyl ketone
Nitric acid, concentrated, 4N, 1:1
Perchloric acid
Potassium pyrosulfate, crystals
Sodium-potassium flux
Sulfuric acid, concentrated
Iron Carrier

Special Apparatus:

Platinum dish, 50-ml
Platinum dish, pellet size
Turner Fluorometer (Note 1 for operating instructions)
Propane torch

* See appendix A

Preparation of Sample:

A. Soil and Sediments

Total dissolution of sample is sometimes a rather difficult and lengthy process but analogous to the procedure for dissolution of thorium sediments given elsewhere in this manual. After dissolution, continue at C, (b), step 1.

B. Air Filters

Depending on the residue on the filter, the sample may subsequently need treatment as a sediment sample with extraction of uranium. At first, depending on filter type, the sample is treated as follows:

(a) Nylon Mesh Membrane

1. Fold the filter into a 250-ml beaker and add 30 ml concentrated nitric acid plus 5 ml sulfuric acid.
2. Digest on a hot plate, slowly evaporating the nitric acid.
3. Allow the remaining sulfuric acid to char some of the organic material, then cautiously add more concentrated nitric acid until brown fumes have vanished,
4. Repeat steps 2 and 3 until no more charring occurs and no more nitric acid decomposes.
5. Transfer the material to a small platinum dish (50 ml). Evaporate to fumes of sulfuric acid, and then to dryness. If the amount of residue is very small, proceed here/ Otherwise, treat sample as soil or sediment. (Iron carrier may have to be added.)
6. Add 5 ml concentrated hydrofluoric acid and 2 ml perchloric acid cautiously and evaporate to dryness.
7. Evaporate to dryness twice in the presence of 2 ml concentrated nitric acid.

8. Add 20 ml 4N nitric acid, warm to dissolve, and transfer to a 50-ml volumetric flask with 4N nitric acid. Continue at C.
9. If insoluble residue remains after step 8, a pyrosulfate fusion may be necessary followed by hydroxide precipitation. See soil and sediment dissolution procedure.

(b) Membrane Filters without Nylon

1. Digest the filter for a short time with a mixture of 5:1 nitric: perchloric acid in a covered Teflon beaker. Hotplate on low.
2. Evaporate until about one-third of original volume of perchloric acid remains.
3. Add 5 ml concentrated hydrofluoric acid to the perchloric acid mixture and evaporate to fumes of perchloric acid and then to dryness.
4. Add 20 ml 4N nitric acid and warm to dissolve. Transfer to a volumetric flask with 4N nitric acid and dilute to volume with 4N nitric acid. Continue at C.

C. Water

Initially, an incoming water sample can be filtered and a 0.25-ml aliquot taken, evaporated into a platinum dish, and analyzed directly for uranium. If the first fluorometric analysis indicates too large a suppression of fluorescence, treat the sample as an effluent.

(a) Total Sample Analysis

Shake sample thoroughly and remove a 10-ml aliquot. Centrifuge or filter and run two separate analyses for water and sediments, or evaporate the aliquot to dryness and treat as a sediment. If the amount of sediment is small, the treatment described for membrane filters without nylon might do.

(b) Effluents (High in Dissolved Solids)

The following procedure eliminates most interference with exception of large quantities of iron with chloride and perhaps sulfate and chlorate which carry over into the organic. Try total sample analysis if high suppression is encountered after extraction. (Anion interference may be removed by precipitation of uranium on 1-2 mg ferric ion from about 30 ml at pH 9.)

1. Pipet a 20-ml aliquot to a 50-ml screw cap ketone-resistant plastic centrifuge tube.
2. Add 0.5 ml concentrated nitric acid if sample is not made up in 4N acid.
3. Add 20 ml aluminum nitrate salting solution to tube and mix well immediately.
4. Add 10 ml methyl isobutyl ketone accurately with pipet.
5. Cap tube firmly but not too tight. Check for leaks.
6. Shake tube for 3 minutes.
7. Centrifuge 5 minutes to separate phases cleanly.
8. Pipet a 100 λ to 250 λ aliquot from the upper ketone layer into the small platinum fluorometry dish and evaporate to dryness gently under an infra-red lamp. Gently flame the dish until the organic residue has disappeared.

Preparation of Sample Pellet and Analysis:

1. Mount a propane torch so that the flame will project straight up. Ignite torch and allow to burn at low flame until valve region becomes warm whereupon a less variable, more controllable small flame will be had.
2. Mount an adjustable guide, such as a ring, about 2 inches above the torch as a rest for the platinum or nichrome heavy-gauge wire dish holder.

3. Place the platinum dish in the wire holder and scoop in an over-flowing amount of flux. Level off the excess.
4. Fuse over a low flame, adjusting the height of the ring so that complete fusion takes place in about 30-45 seconds.
5. Allow melt to partially solidify and reheat, swirling gently as last particles liquify. Circle edge of dish over flame. Avoid heating to visible redness in ordinary room light.
6. Remove dish from flame and allow to solidify completely. Allow to cool for a few minutes (Store in dessicator if necessary.)
7. Establish background fluorescence of pellet (F_B) as per Note 1. Handle pellet with tweezers and avoid chipping.
8. Return the pellet to the dish containing the dried sample aliquot, and establish the new fluorescence (F_2) after repeating steps 4-6.
9. Rinse the dish in 1:1 nitric acid and water and dry it.
10. Pipet in 0.1 ml uranium standard * and evaporate.
11. Return the pellet to the dish and obtain a third fluorescence (F_3) as per steps 3-6.
12. Clean the dish by dipping in fused potassium pyrosulfate and digesting for 30 minutes in 1:1 hot nitric acid.
13. With each series of samples run at least three standards pellets: that is, establish three successive fluorescence (1 background plus 2 successive standard additions) for 3 different pellets.
14. Consider the data obtained thus far;

If $F_2 < F_B$ treat sample as an effluent and repeat analysis.

The terms quenching or suppression refer to the ability of foreign substances to inhibit uranium fluorescence. In a few

*Two uranium standards are prepared (4.00 and 0.400 g/l). Generally select that amount whose fluorescence is greater than that appearing for the sample.

cases where the sample fluorescence approaches the magnitude of the background, and high quenching effects are taking place, consideration of background quenching might have to be made to avoid low results.

- (a) The sample can be extracted to remove interferences; or,
- (b) Correct the background for quenching. (See Alternate Method.)

Calculation of Uranium:

The procedure just described makes unnecessary consideration of pellet weight variation as well as presence of small amounts of uranium fluorescence inhibitors. These effects are also operative on the internal standard added to the sample and the net effects cancel out.

$$(a) \quad \mu\text{g U/pellet} = \frac{F_2 - F_B}{F_3 - F_2} \times \text{g U standard}$$

$$\mu\text{g U/sample} = \text{g/pellet} \times \text{dilution and/or aliquot factor}$$

- (b) Empirical Correction Factor

For each of the standards* calculate ΔF where

$$\Delta F = \frac{F_3 - F_2}{F_2 - F_B}$$

Then find the average $\bar{\Delta F}$ for the set of standards. (Note 3.)

- (c) Multiply the result found in (a) by $\bar{\Delta F}$ whenever $\bar{\Delta F}$ differs significantly from 1.00.

$$\mu\text{g/sample} \times \bar{\Delta F} = \text{corrected } \mu\text{g/sample}$$

*The two added quantities must be identical.

Alternate Method:

This method overcomes the problem of re-heating the pellet for the third time as well as patience required to prepare pellets of identical weight. Pellet weight variations may be rather large, an internal standard need not be determined, and a ΔF factor need not be calculated. This method attempts to simplify analysis of a large number of samples with the restriction that quenching is not accounted for. (cf. fresh water samples and many samples extracted by methyl isobutyl ketone.)

At least one series of determinations should be made using the internal standard; the net fluorescences of standards alone are plotted against pellet weight in mgs on linear graph paper. The best straight line is drawn through the points; use the points lying nearest the line for the following:

Select the sample having the lowest weight as the "normal pellet." Determine the correction factor necessary to raise the observed fluorescence of the remaining standards to the fluorescence of the "normal pellet" and plot this factor against the respective pellet weight on two cycle semi-log paper. The resulting line is used to normalize future F readings (background subtracted) to a common pellet weight. At least three standard pellets should be run identically with each set of unknowns and averaged.

Calculations:

$$(F_2 - F_B) \text{ normalize} > F^*$$

$$\frac{F^* \text{ sample}}{F^* \text{ standard}} \times \mu\text{g U standard} \times \text{dilution factor} \\ (\text{aliquot}) = \mu\text{g U/sample}$$

Supplementary Calculation:

To correct for background quenching, it is necessary to determine a suppression factor:

For the three standards run with the unknowns, normalize the value $F_2 - F_B$ above to obtain F^* standard. Then, find the average (\bar{F}^* standard) and divide it by μg uranium in the standard.

Similarly, for the sample find the value $\frac{1}{\Delta F} (F_3 - F_2)$ and normalize it to obtain F^* sample standard.

Divide this by μg U added to the sample.

$$\text{The quenching factor is then } Q = \frac{F^*_{ss}/\mu\text{g U added}}{\bar{F}^*_{std}/\mu\text{g U std}}$$

Values of Q from 0.95 to 1.05 are generally disregarded and no correction is necessary. For $Q < 0.95$, substitute QF_B for F_B in the calculation given in "Calculation of Uranium," item (a).

Notes:

1. Operation of the Instrument - Turner Model *110:

- (a) Turn on the unit (activate mercury lamp by forcing slightly full clockwise and release) with the pellet holder door open and allow to warm up for one hour. (Filter 2A-12 on left side; filter 7-60 on right side.)
- (b) Set the meter to zero with the zero control.
- (c) Close the door after having blocked the pellet aperture with some opaque substance (electrical tape).
- (d) Set dial so that scale divisions equal zero and re-zero the meter using the blank knob.
- (e) Repeat steps (b), (c), and (d) at least once for several positions of the meter sensitivity control to obtain meter behavior which is neither too sluggish nor erratic.

- (f) Open door and remove tape and place a background pellet in the sample holder.
 - (g) Close door and rotate fluorescence dial until meter is zeroed. If this is not possible, or if the reading is less than 10, adjust the range selector so that the background falls at about 60 scale divisions or less. The range selector is left permanently in this position (or until a new batch of flux produces pellets giving a significantly different background).
 - (h) Replace background pellet with sample or standard pellet and read the fluorescence at meter zero point. If the needle is off scale to the left indicating higher concentrations, place at $10^{1.0}$ neutral density filter over the yellow filter. If more than $10^{3.0}$ density is required, dilute the sample and repeat analysis.
 - (1) When running a series of pellets, recheck zero setting and blank knob after several determinations.
- 2. If erratic results are gradually obtained on replicate samples, the flux should be suspected as "aging" and a new batch prepared.
 - 3. This factor ($\bar{\Delta}F$) has been found to vary with the age of the flux and its initial value seems to depend on the heating the flux receives when first prepared.

RADIOCHEMICAL DETERMINATION OF THORIUM
IN ENVIRONMENTAL SAMPLES

Principle of the Method:

The sample is solubilized with nitric acid following appropriate concentration and decomposition pre-treatments. Thorium is separated from calcium and sodium by co-precipitation with ferric hydroxide to prevent precipitation of calcium fluoride and sodium aluminum fluoride. Separation from iron, titanium, and zirconium is accomplished by co-precipitation with lanthanum or yttrium fluoride. The thorium is separated from the lanthanum or yttrium for counting or electrodeposition by solvent extraction of the thenoyltrifluoroacetone complex.

Reagents ^{*}:

Nitric acid, concentrated
Iron carrier, 1 mg iron/ml
Iron carrier, 10 mg iron/ml
Yttrium carrier (purified), 15 mg yttrium/ml
Lanthanum carrier, 10 mg lanthanum/ml
Ammonium hydroxide, concentrated
Ammonium hydroxide, 20% solution
Hydrogen peroxide, 30%
Hydrofluoric acid, 48%
Wash solution (6% nitric acid, 3% hydrofluoric acid)
Hydrochloric acid, concentrated
Thenoyltrifluoroacetone (TTA) (10% in xylene)
Thymol blue, 0.1%

* See appendix A

1:1 ammonium hydroxide

Wash solution

0.2N nitric acid

2N nitric acid

Adhesive solution

Apparatus:

Beaker, Teflon

Burner, Mahar

Centrifuge

Mixer, Vortex

Sample Preparation:

A. Water Samples

1. Filter through an 0.45µmembrane filter and stabilize the filtrate by acidifying to 2% with concentrated hydrochloric acid. Note volume filtered and reserve suspended solids for separate analysis.
2. Transfer one liter of filtered water to a 1-liter beaker. Add 20 ml of 14N nitric acid, 10 ml of 10 mg iron per ml carrier solution and 3 ml of 10 mg lanthanum per ml carrier solution. Evaporate to dryness or nearly so on a steam bath or hot plate.
3. Add 10 ml of 14N nitric acid and 100 ml of water. Cover and heat until the residue has dissolved. Proceed with the hydroxide separation.

B. Sediment and Soil Samples

1. Weigh one gram of sample dried and ground to pass a 100-mesh sieve into a porcelain crucible and ash overnight at 550°C.
2. Transfer sample to a 100-ml Teflon beaker and evaporate twice to dryness with 10-ml portions of concentrated hydrochloric acid,
3. Dry in oven at 100°C for 2 hours or overnight to dehydrate silica.
4. Add 2 ml of concentrated hydrochloric acid and 20 ml of water and heat while covered for 30 minutes, Decant liquid into a 40-ml centrifuge tube. Centrifuge at 2000 rpm for 5 to 10 minutes. Decant supernatant liquid into a 250-ml centrifuge bottle and transfer the residue to the Teflon beaker.
5. Add 15 ml of 48% hydrofluoric acid and 10 ml of concentrated hydrochloric acid to the residue and evaporate to dryness on a hot plate. Remove fluoride by three successive evaporations to dryness with 5-ml portions of 6N hydrochloric acid.
6. Add 2 ml of concentrated hydrochloric acid and 20 ml of water, Cover and heat for 30 minutes and then transfer to the same 50-ml centrifuge tube used in step 4. Centrifuge and decant supernatant liquid into the centrifuge bottle containing the first dissolved portion. Transfer the remaining residue to a 50-ml platinum dish, add 5 ml of concentrated hydrochloric acid and 5 ml of 48% hydrofluoric acid and evaporate to dryness.
7. Add one gram of potassium pyrosulfate to the platinum dish and fuse over a Mahar burner. Cool, add 2 ml of concentrated hydrochloric acid and 20 ml of water, and heat until residue has dissolved. Combine with the other dissolved portions in the 250-ml centrifuge bottle.

8. Add one ml of 10 mg iron per gm sample. If less than one gram of sample was taken, add an additional one ml of iron carrier for each 100 mg of weight below 1 gram. Proceed with the hydroxide separation of thorium.

C. Air-Borne Dust and Suspended Solids Collected on Membrane Filters

1. If the solids weigh from 0.1 to 1 gram, ignite in a porcelain crucible or dish and proceed as for sediment and soil samples. If the weight is less, wet ash the filter in a covered 150-ml borosilicate beaker with repeated additions of 14N nitric acid in the presence of one ml of concentrated sulfuric acid.
2. Transfer solution and residue to a 50-ml platinum dish, add 5 ml of 48% hydrofluoric acid, evaporate until the fumes of sulfuric acid are given off, add 1 gram of potassium pyrosulfate, heat to volatilize sulfuric acid and fuse the pyrosulfate. Dissolve the residue in 3 ml of 14N nitric acid and 20 ml of water, transfer to a 250-ml centrifuge bottle, add 10 ml of 10 mg iron carrier per ml and proceed with the hydroxide separation of thorium.

Procedure:

A. Hydroxide Separation of Thorium

1. Transfer sample to a 250-ml centrifuge bottle and, while swirling, add concentrated ammonium hydroxide from a burette to incipient precipitation of the iron (permanent amber color). Increase the volume to about 190 ml by adding distilled water and then add 15 ml of concentrated ammonium hydroxide slowly while mixing. Allow to stand one hour and centrifuge at 1800 rpm. Decant and discard the supernatant liquid.

2. Add 10 ml of concentrated nitric acid to the beaker which had contained the sample, cover, and heat on a hot plate until the acid refluxes to the top of the beaker. Cool and wash down the sides of the beaker with about 10 ml of water.
3. Pour the diluted acid from the beaker into the centrifuge bottle in such a way as to wash down the sides of the bottle and transfer the remaining acid from the beaker to the bottle with several water washes. Swirl the centrifuge bottle to dissolve the precipitant and dilute to about 100 ml.
4. Add concentrated ammonium hydroxide from a burette to incipient precipitation, dilute to about 190 ml, and add 10 ml of concentrated ammonium hydroxide slowly with mixing. Allow to stand one hour and centrifuge at 1800 rpm. Decant and discard the supernatant liquid.
5. Slurry the precipitate by striking the bottle against the heel of the hand and then add water to 200 ml. Centrifuge at 1800 rpm. Decant and discard the wash.
6. Using a pipet, add 3 ml of concentrated nitric acid to the centrifuge bottle in such a way that the precipitate adhering to the sides will dissolve. Swirl the bottle to dissolve the precipitate. If the precipitate fails to dissolve completely, add 10 drops 30% hydrogen peroxide.

B. Fluoride Separation of Thorium

1. Transfer the solution and any precipitate of silica from the centrifuge bottle to a 50-ml polypropylene centrifuge tube with distilled water and dilute to about 30 ml. If

lanthanum or yttrium carrier were not previously added, add at this point and mix.

2. Add 5 ml of 48% hydrofluoric acid, mix, and allow to stand for one hour.
3. Centrifuge at 1600 rpm for 5 minutes. Decant and discard the supernatant liquid.
4. Disperse the precipitate with the Vortex mixer in 5 to 10 ml of a wash solution containing 6% nitric acid and 3% hydrofluoric acid and centrifuge at 1600 rpm. Decant and discard the wash solution.
5. Repeat step 4.
6. Add about 5 ml of concentrated nitric acid to the precipitate, disperse with the Vortex mixer and pour into a 30-ml Teflon beaker. Repeat with a second 5-ml portion of nitric acid and then with two 5-ml portions of water. Add 1 ml of 70% perchloric acid and evaporate on a hot plate overnight. The residue generally will not go completely to dryness.
7. Add 2 ml of concentrated nitric acid and evaporate nitric acid on a hot plate. Repeat with 2 ml more of nitric acid.
8. Add 5 ml of 2N nitric acid, cover, and heat for 10 minutes to dissolve the residue.

C. Extraction of Thorium with Thenoyltrifluoroacetone (TTA)

1. Add the amount of freshly-prepared ascorbic acid solution which will decolorize 5 mg of iron and then add one drop of 0.1% thymos blue. Adjust to pH 2.0 (salmon pink color) with 1:1 ammonium hydroxide and 2N nitric acid. Make the final

adjustment with 0.5N ammonium hydroxide and 0.5N nitric acid.

2. Transfer the sample to a 125-ml separatory funnel with a wash solution at pH 1.5 (adjust 0.1N nitric acid to pH 1.5 with ammonium hydroxide using a pH meter). Use enough wash solution to end up with 15 ml total volume.
3. Add 15 ml of 10% TTA in xylene and shake for fifteen minutes. Drain off and discard the aqueous layer.
4. Add 5 ml of 0.2N nitric acid to the organic layer and shake for five minutes. Drain off and discard the aqueous layer. Repeat this wash step with two additional 5-ml portions of 0.2N nitric acid.
5. Add 15 ml of 2N nitric acid to the organic layer and shake for fifteen minutes to strip the thorium from the organic layer. Drain the aqueous layer into a 30-ml borosilicate beaker. Repeat the stripping with a second 15-ml portion of 2N nitric acid.
6. Add 1 ml of 70% perchloric acid to the beaker and evaporate to dryness on a hot plate.

D. Mounting of Thorium for Alpha Counting

1. Add 2 ml of concentrated nitric acid to the beaker, cover, and digest for 20 minutes,
2. Add 1 ml of iron carrier (1 mg iron/ml) to 30-ml Teflon beaker retained above. Transfer the solution from step 1 into the Teflon beaker and adjust the volume to 15 ml,
3. Add 10 ml of 1:1 ammonium hydroxide slowly by burette while stirring. Cover and let stand for one hour,

4. Prepare a planchet by cleaning in 1:1 nitric acid and drying. Add about 14 drops of adhesive solution to planchet and spread over entire surface. Let stand until the solvent has evaporated.
5. Stir and filter the solution in the beaker on a membrane filter apparatus using .45 micron-47 mm membrane filters. (Wet filter prior to filtering sample.) Wash beaker and filter funnel with 5% ammonium hydroxide.
6. Remove funnel top. Carefully place membrane filter on planchet. Use stirring rod to press around outside edge to seal filter to planchet. Place planchet in drying oven at 80-105°C for at least two hours prior to counting. If possible, dry overnight.

E. Calculations

$$\frac{R_s - R_{bkg}}{A \times B} = \text{pCi } ^{230}\text{Th/sample} \quad \frac{\text{pCi Th/sample} - C}{D} = \text{pCi } ^{230}\text{Th/liter}$$

R_s = alpha count rate of sample (c/m)

R_{bkg} = alpha counter background (c/m)

A = calibration factor obtained by counting a known amount of thorium-230 mounted as described above.

B = yield

C = sample blank (pCi) calculated by using equation for pCi Th/sample

D = sample volume in liters

THE APPARATUS AND METHOD FOR RADON TRANSFER

Principle of the Method:

The object of this procedure is to describe the apparatus and method necessary to transfer the radon-222 gas produced in the solution containing the radium-226 to the scintillation chamber.

Many variations of the procedure and apparatus described herein could be used; however, the system has been used for routine analysis and it has proved to be satisfactory.

Reagents*:

Air, compressed (Note 1)

Apparatus:

The specification for the transfer apparatus is illustrated in Fig. 11. The use of glass joints with O-ring seals is recommended because the O-ring seals decrease the amount of stopcock grease necessary to seal the joints.

Procedure:

1. Attach a scintillation chamber to the manometer by means of a flat, O-ring, sealed glass joint.
2. Attach a bubbler tube containing the sample solution to an ascarite-drierite drying tube with a short length of rubber tubing. The drying tube is attached to a short length of thermometer tubing with rubber tubing.

*See appendix A

3. Stopcock 1 is opened and a vacuum is applied to the system.
4. When the left-hand leg of the U-tube manometer has reached its maximum height, close stopcock 1.
5. The system should be left in this configuration for three to five minutes. If the mercury begins to drop in the left-hand leg of the manometer, check the glass joints and rubber tubing connections for leaks. Apply a very light coating of Dow-Corning silicon grease to the connections if necessary, then repeat steps 4 and 5.
6. Open stopcocks 1 and 2 and permit the mercury in the left-hand leg of the manometer to reach its maximum height. Close stopcock 1 and check for leaks as in step 5.
7. Connect the dry aged air tank with gum rubber tubing. The air pressure should be limited to one or two pounds of pressure. A needle valve between the air tank regulator and the bubbler is recommended.
8. Open stopcock 3 slowly to prevent a pressure surge. Open stopcock 4 using the same precaution.
9. The air pressure will have to be increased occasionally to keep the flow through the bubbler fairly constant.
10. The flow of aged air through the bubbler should be controlled so that the transfer reaches completion with 25-30 minutes.
11. The mercury in the left-hand leg of the manometer will begin to drop as the air is passed through the bubbler. When the level of the mercury in both legs of the manometer is equal, shut off stopcocks 4, 3, and 2 in that order.
12. Remove the scintillation chamber and place in a light-tight cabinet for the 6-hour ingrowth period.

13. Remove the purged bubbler and desiccant. The system is ready now for the next sample.

Note 1: Hold for 90 days before using, and leave 25-50 pounds gauge pressure in cylinder.

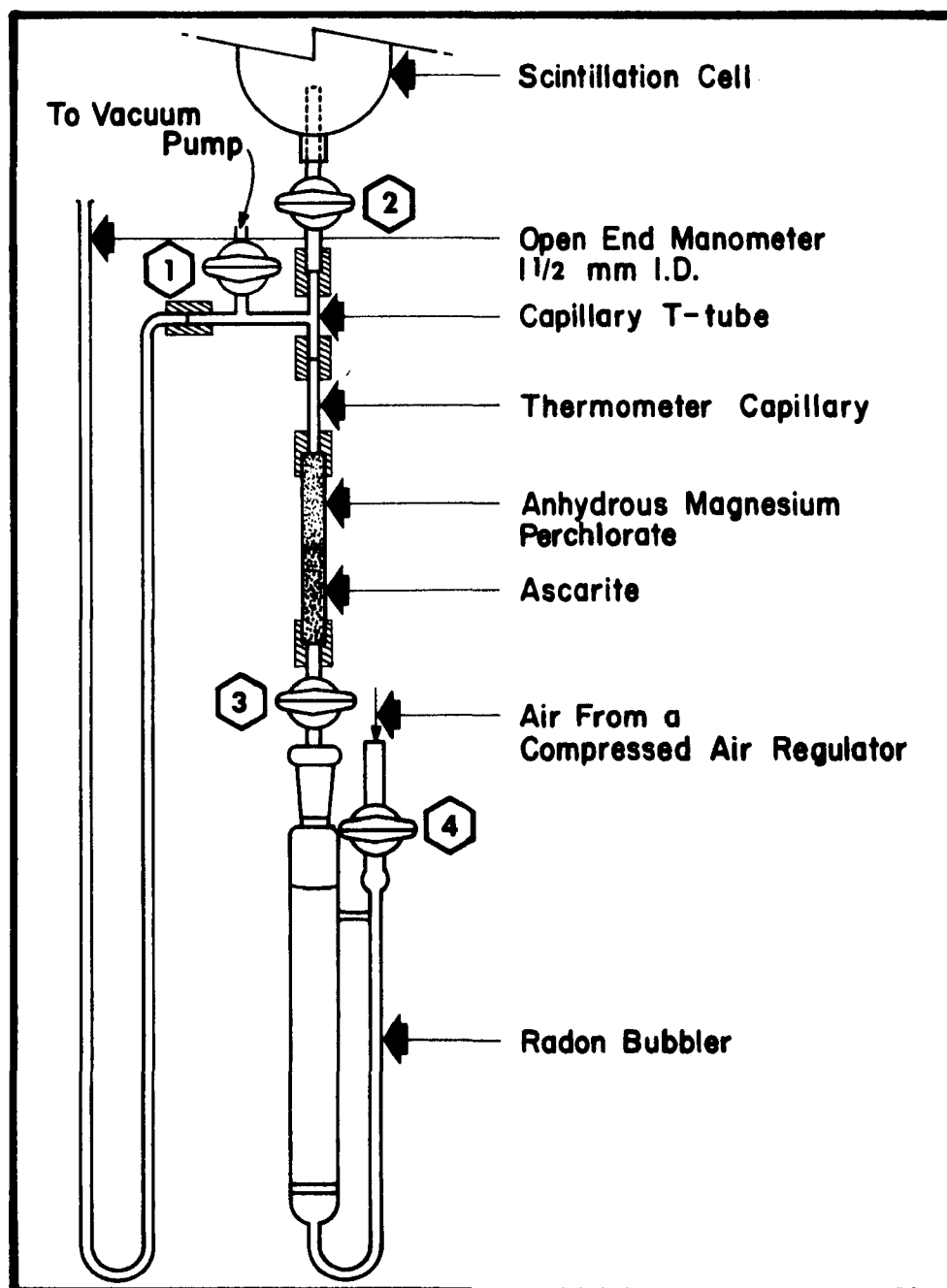


Figure 11
Apparatus for Radon Transfer

CONSTRUCTION OF SCINTILLATION CHAMBERS
FOR DETECTING RADON GAS

Principle of the Method:

Radium-226 can be determined by counting the alpha emissions of radon-222. In order to detect the alpha emissions of radon-222, suitable scintillation chambers are needed. This report illustrates one solution to this problem.

Materials:

1. Kovar cups, 196" O.D., 3" length after trimming,
Catalog #942003, Model DKC #5W
Source: The Carborundum Company, Refractories Division
Latrobe Plant, Latrobe, Pennsylvania
2. Quartz glass windows, 2" x 1/8" commercial grade
Source: Engelhard Industries, Inc., Amersil Quartz
Los Angeles, California
3. Phosphor, silver activated zinc sulfide, Helecon fluorescent
pigments, Color #2205, Lot #H-263
Source: United States Radium Corporation
East Hanover Avenue, Morristown, New Jersey
4. Stopcocks, 2 mm, standard taper, #7280 or #7544
Corning Glass Works
5. Joint, O-ring #33650
Kimble #33650

6. Chemicals:

Butyrate dope, clear #22

Source: The Testor Corp., Rockford, Ill.

Acetone, analytical grade

Source: J. T. Baker Chemical Co., Phillipsburg, New Jersey

Amyl Acetate, purified, Lot #20,545

Source: J. T. Baker Chemical Co., Phillipsburg, New Jersey

Epoxy resin, bond agent R-313

Source: Carl H. Briggs Co., 1547 Fourteenth Street
Santa Monica, California

Stannous Chloride, reagent grade, lot #20493

Source: J. T. Baker Chemical Co., Phillipsburg, New Jersey

Krylon Clear Spray Coating, crystal clear, #1302

Source: Krylon Inc., Norristown, Pennsylvania

Metal Operations on the Kovar Cups:

The Kovar cups have a rough edge in their initial form. It is necessary to trim the rough edge off on a lathe. A finished length of 2 13/16" and 3" will give internal volumes of 100 and 125 ml, respectively. The edge is machined perpendicular to the wall of the cup. A 13/32" hole is drilled in the center of the dome of the cup. This operation is also performed with a lathe. After the machining and drilling operations, there is a burr at the edges. This burr is filed off. A length of 3/8" O.D. copper tubing is cut into 1" sections. These 1" sections are placed flush with the inside edge of the hole in the Kovar cup and silver soldered. An excess of heat must be avoided to solder this joint because both the Kovar and copper are easily melted and oxidized. The soldering operation is also done in a lathe so that the copper tubing will be square with the top of the Kovar cup. It may also be necessary to ream out the copper tube so that the glass tube of the stopcock will fit.

The soldered joint is smoothed with file and sandpaper, and both the interior and exterior surfaces of the cup are polished to a high luster with steel wool.

The chambers are thoroughly cleaned in an ultrasonic cleaner. Ultrasonic cleaning is not necessary; the important point is to remove all traces of oil and grease from the chambers.

Coating the Inner Surfaces of the Chamber with Silver Activated Zinc Sulphide:

The application of the phosphor to the inner surfaces of the Kovar cup is a critical step in the construction of the chambers.

An old phonograph turntable is revamped to hold the chamber by the copper tube. The turntable is positioned at a 45° angle and run at its lowest speed (approximately 33 rpm).

The silver activated zinc sulfide is made into a slurry in order to spray it into the chambers. The slurry is made according to the following formulation:

<u>silver activated zinc sulphide</u>	<u>acetone</u>	<u>amyl acetate</u>	<u>butyrate dope</u>
50 gms	200 ml	100 ml	10 ml

This is enough material for about ten chambers.

The butyrate dope is the bonding agent, the amyl acetate is the carrier and the acetone speeds the drying of the slurry. The above ratios are not strict and, in fact, should be varied until the desired results are obtained.

The chamber is wiped and blown out with air. The chamber is weighed, a small cork is placed in the cup end of the copper tube, and the chamber is placed on the turntable. The slurry is thoroughly mixed and a portion of the slurry is transferred to the jar of a Model C Thayer & Chandler air brush. The compressed air for the air brush is supplied from a tank of aged dry air. The air pressure is twenty-five pounds.

The turntable is turned on and the spraying operation begun.

The phosphor must be applied in a series of many thin coats working from the top edge down. A coat is applied to the chamber, and then it is dried with air from the air brush. This procedure is repeated until the desired amount of phosphor has been applied to the chamber. The slurry in the jar of the air brush must be shaken every twenty to thirty seconds to prevent the slurry from settling out. The chambers should have a minimum of 15 mg/cm of silver activated zinc sulphide which amounts to approximately 2.5 gms of silver-activated zinc sulphide per chamber.

The silver-activated zinc sulphide coating should not have a large grain texture and it should not be allowed to run. The coating should be evenly distributed over the inside surface. If the silver-activated zinc sulphide is grainy or runs, it can be removed with acetone and re-applied.

The cork is removed from the copper tube and the chambers are dried overnight in a drying oven at 80°C. After drying, the open end of the chamber is struck sharply on a table top to check the bonding of the silver-activated zinc sulphide to the Kovar cup walls. If the phosphor comes off the wall, the phosphor must be removed with acetone and re-applied with a higher percentage of butyrate dope in the slurry.

When the bonding is acceptable, the chamber is weighed to determine the amount of phosphor in the chamber. If more phosphor is needed, it can be applied directly on the dry phosphor in the chamber.

Deposition of Tin Oxide on the Quartz Windows:

Reagent grade stannous chloride is placed in a small evaporating dish. The dish is put on a stand which is positioned over a Fisher burner. A previously cleaned 2" by 1/8" commercial grade quartz glass window is heated over a blast burner and placed in the fumes given off by the hot stannous chloride. The stannous chloride should be placed in a hood but air turbulence must be kept to a minimum. The tin oxide that is deposited on the window should be as uniform as possible.

The quartz glass window is again heated over a blast burner until the coating turns black. The tin oxide is wiped off with tissue paper and the window is again placed in the fumes given off by the stannous chloride. This will usually give a uniform coat of tin oxide on the window. The uniformity and amount of tin oxide on the window can be checked by reading the resistance across the diameter of the coated surface of the window with an ohm meter. The coated surface should have a maximum resistance of 100,000 ohms. The tin oxide coating on a properly coated window is not visually detectable.

The purpose of the tin oxide is to have a conducting film on the window so that a surface charge will not build up on the window from the ionization

Do not touch the coated surface of the window.

Sealing the Chamber:

Two mm standard taper pyrex stopcocks with O-ring joint attached are placed in the copper tube of the chamber. The stopcocks are attached to tube with Bonding Agent R-313. The exterior surface of the Kovar cup is coated with Krylon clear coating. Do not coat exposed surface of quartz glass window (see Fig. 12).

Determining the Background and Standardizing the Chambers:

The chambers are evacuated with a vacuum pump, flushed with dry, aged air and re-evacuated. This procedure is repeated until the background has attained a constant minimum value.

A ten-pico solution from a National Bureau of Standards radium-226 solution was used to standardize the chambers. The radium-226 solution is sealed in an emanation tube for 28 days to permit the radium and its daughters to reach equilibrium. The chambers have a counting range of 4.70 to 5.20 counts per micromicrocurie of radium-226 after the radon-222 has ingrown in the scintillation chamber for six hours. A record should be kept of the relative efficiency of each chamber.

It is important to de-gas the chamber after the sample has been counted in order that the chamber background will not be increased. It is also necessary to keep moisture out of the chambers.

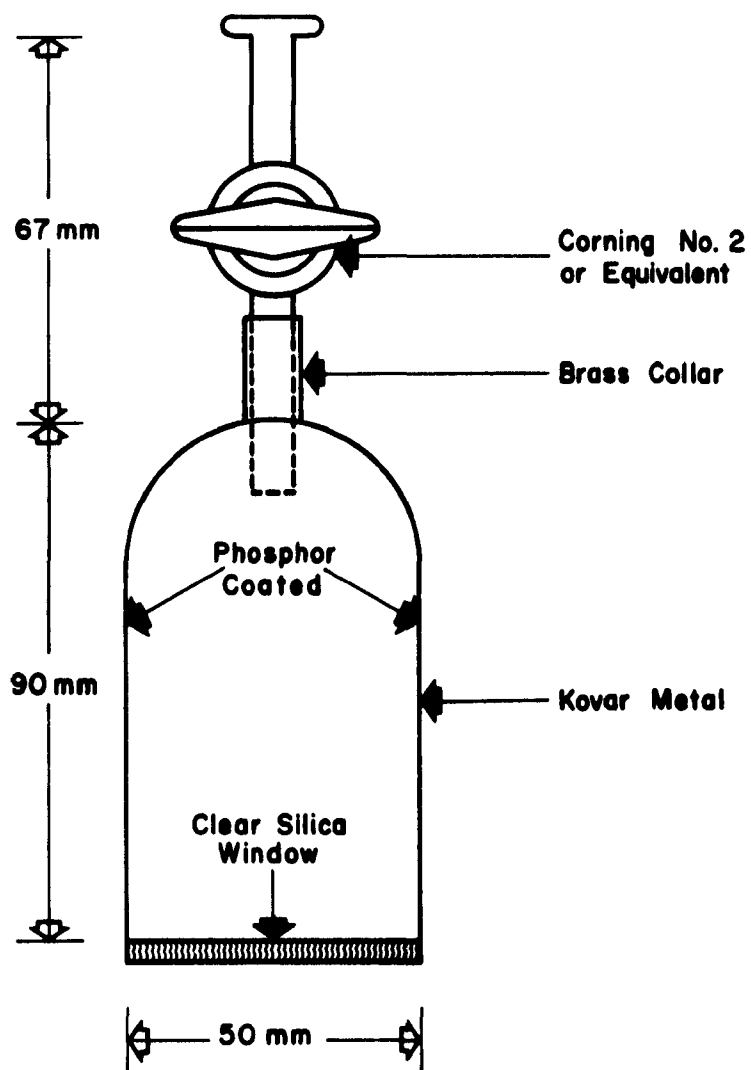


Figure 12
Lucas Scintillation Cell

APPENDIX A

Acetic Acid

6N - Add 345 ml glacial acetic acid to 500 ml distilled water and dilute to 1000 ml.

Alcohol-hydrochloric Acid

Add 10 ml concentrated hydrochloric acid to 100 ml absolute ethyl alcohol.

Ammonium Acetate

6N - Dissolve 482.6 g ammonium acetate (FW 77.1) in 800 ml distilled water. Dilute to 1000 ml with distilled water.

Ammonium Acetate Buffer, 5.2 pH

Dissolve 153 g ammonium acetate (FW 77.1) in 900 ml distilled water, add 28.6 ml of glacial acetic acid. Adjust to pH 5.2 using either ammonium hydroxide or acetic acid. Dilute to 1000 ml with distilled water.

Ammonium Carbonate

Saturated Solution - Dissolve 110 g ammonium carbonate in 100 ml of distilled water. An excess of ammonium carbonate should be visible.

Wash Solution - Dilute 50 ml of the saturated solution to 1000 ml with distilled water.

Ammonium Dichromate

1.0M - Dissolve 252 g of ammonium dichromate (FW 252.1) in distilled water. Adjust pH to 6.5 with ammonium hydroxide and/or nitric acid, and dilute to 1000 ml with distilled water.

0.1M - Same as 1.0M only use 25.2 g of ammonium dichromate.

Ammonium Hydroxide

Concentrated, 15N

6N - Dilute 400 ml concentrated ammonium hydroxide to 1000 ml with distilled water.

Ammonium Sulfate

10%w approx. - Dissolve 10 g ammonium sulfate in 100 ml distilled water.

Complexing solution

Dissolve 216 g of 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 5.20 using approximately 70 ml 6N ammonium hydroxide, dilute to 3 liters with water. (Re-check pH before using,)

Dowex 2-X8 20-50 mesh

40 ml of the resin is washed with 150 ml water and transferred to anion column.

50W-X8 - 85 ml of the resin is transferred with water to the cation column. The resin is charged with 500 ml 4 N sodium chloride and 250 ml water at flow rate of 10 ml/min.

Ether-hydrochloric Acid

In an ice-bath, add equal volumes of concentrated hydrochloric acid and diethyl ether.

Nitric-perchloric Acid

Prepare by adding 162 ml 70% perchloric acid to 838 ml concentrated nitric acid.

Ethylenediaminetetraacetate, Disodium

EDTA, disodium - Dihydrate, powder.

3%w - Dissolve 33.3 g of disodium EDTA in 900 ml of distilled water, adjust to pH 5.2 with ammonium hydroxide and dilute to 1000 ml with distilled water. The pH is rechecked just prior to using.

6% - Dissolve 60 g disodium EDTA in 900 ml water and dilute to 1 liter.

2% - Dissolve 20 g disodium EDTA in 900 ml water and dilute to 1 liter.

Formalin

Formaldehyde solution 36-38%.

Hyamine-methyl Alcohol

Hydroxide of hyamine 10-X, 1M in methyl alcohol.

Hydrochloric Acid

Concentrated (12N)

6N - Add 500 ml concentrated hydrochloric acid to 900 ml water. Dilute to 1 liter.

1.5N - Add 125 ml concentrated hydrochloric acid to 900 ml water. Dilute to 1 liter.

3N - Add 250 ml concentrated hydrochloric acid to 900 ml water. Dilute to 1 liter.

Hydrogen Peroxide

30%w

3% - Dilute 100 ml 30% hydrogen peroxide to 1000 ml with distilled water.

Hydrofluoric Acid

48%

Hydroxylamine Hydrochloride

5% - Dissolve 5 g hydroxylamine hydrochloride in 95 ml 95% ethyl alcohol and dilute to 100 ml.

Liquid Scintillation Solution (tritium)

Dissolve 8.0 g 1,5 diphenyloxazole (PPO), 1.5 g p-BIS-(methystyrl)-benzene (BIS-MSB), and 120 g napthalene in 900 ml spectrographic grade p-dioxane and dilute to 1 liter. Store in amber bottle. The solution is not usable after one month.

Liquid Scintillation Solution (carbon-14)

Dissolve 1.5 g 1,5 diphenyloxazole (PPO) and 300 mg 1,4-bis-2(4-methyl-phenyloxazole)-benzene (dimethyl-POPOP) in 900 ml toluene and dilute to a liter with toluene. Store in an amber bottle. The solution is not usable after one month.

Nicholson's Flux

Weigh - 65.8 g potassium carbonate
50.5 g sodium carbonate
33.7 g sodium tetraborate-decahydrate
30 mg barium sulfate
into a 500-ml platinum dish. Mix and fuse. Coll and grind to pass a 10-mesh screen.

Nitric Acid

Concentrated

1N - 67 ml concentrated nitric acid is added to 900 ml water, cooled, and diluted to 1 liter with water.

8N - 536 ml concentrated nitric acid is added to 900 ml water, cooled, and diluted to 1 liter with water.

3N - 191 ml concentrated nitric acid is added to 900 ml water, cooled, and diluted to 1 liter with water.

Phosphoric Acid, concentrated

Potassium Hydroxide

5N - Dissolve 280 g potassium hydroxide in 900 ml boiled, distilled water and dilute to one liter.

Silver Nitrate

Chloride test - Dissolve 20 g in one liter of chloride-free water.

Sodium Acetate Buffer

pH 3.6 - Dissolve 200 g sodium acetate in 500 ml water. Add 385 ml acetic acid. Adjust pH 3.6 with ammonium hydroxide. Dilute to one liter.

Sodium Carbonate FW 105.99

Anhydrous, granules

3N or 1.5M

Dissolve 159 g sodium carbonate in 900 ml water, and dilute to one liter.

Sodium Chloride

1.5N - Dissolve 88 g sodium chloride in 900 ml water and dilute to one liter.

4N - Dissolve 234 g sodium chloride in 900 ml water and dilute to one liter.

Sodium Chromate

1N - Dissolve 162 g sodium chromate FW-161.97 in 900 ml water and dilute to one liter.

Sodium Hydroxide

Pellets

6N - Dissolve 24 g sodium hydroxide in boiled water and dilute to 100 ml with the same water.

Potassium Hydroxide

5N - Dissolve 280 g potassium hydroxide in 900 ml boiled, distilled water and dilute to one liter.

Sulphuric Acid

Concentrated (18N)

1N - To 800 ml distilled water, add 55.6 ml concentrated sulphuric acid. Cool, dilute to 1000 ml with distilled water.

0.5%w - To 800 ml distilled water, add 5.0 g concentrated sulphuric acid. Cool, and dilute to 1000 ml with distilled water.

CARRIERS:

Strontium

40 mg/ml - Dissolve 96.6 g strontium nitrate in 800 ml distilled water, dilute to 1000 ml with distilled water.

Standardization:

Pipet 5 ml of carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Make alkaline with ammonium hydroxide and heat to near boiling in a water bath. Add 10 ml 1N ammonium

oxalate, and cool in an ice bath. Filter the solution through a tared, scintered glass filter or Millipore Type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

Lead

100 mg Pb^{+2} /ml - Dissolve 159.9 g lead nitrate in 800 ml distilled water, and dilute to 1000 ml.

Calcium

2M - Dissolve 328.2 g calcium nitrate in distilled water, dilute to 1000 ml.

Barium

40 mg/ml - Dissolve 38.1 g barium nitrate in 900 ml distilled water, dilute to 1000 ml.

10 mg/ml - Use 19.0 g barium nitrate

5 mg/ml - Use 9.5 g barium nitrate

1 mg/ml - Use 1.9 g barium nitrate

Yttrium

1 mg/ml

Standardization:

Pipet 5 ml carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Add 10 ml 2N oxalic acid, and adjust the pH to 1.5 with

concentrated ammonium hydroxide. Heat to near boiling in a water bath; then cool in an ice bath for 20 minutes. Filter the solution through a tared, sintered-glass filter or Millipore Type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol, and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$.

APPENDIX B

Y-90 Decay and Ingrowth Factors (0-72 Hours)

t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$	t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$	t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$
0.0	1.0000	.0000	24.0	.7717	.2283	48.0	.5955	.4045
0.5	.9940	.0054	24.5	.7676	.2324	48.5	.5923	.4077
1.0	.9893	.0107	25.0	.7634	.2366	49.0	.5891	.4109
1.5	.9839	.0161	25.5	.7593	.2407	49.5	.5860	.4140
2.0	.9786	.0214	26.0	.7552	.2448	50.0	.5828	.4172
2.5	.9734	.0266	26.5	.7512	.2488	50.5	.5797	.4203
3.0	.9681	.0319	27.0	.7471	.2529	51.0	.5766	.4234
3.5	.9629	.0371	27.5	.7431	.2569	51.5	.5735	.4265
4.0	.9577	.0423	28.0	.7391	.2609	52.0	.5704	.4296
4.5	.9526	.0474	28.5	.7351	.2649	52.5	.5673	.4327
5.0	.9474	.0526	29.0	.7311	.2689	53.0	.5642	.4358
5.5	.9423	.0577	29.5	.7272	.2728	53.5	.5612	.4388
6.0	.9373	.0627	30.0	.7233	.2767	54.0	.5582	.4418
6.5	.9322	.0678	30.5	.7194	.2806	54.5	.5552	.4448
7.0	.9272	.0728	31.0	.7155	.2845	55.0	.5522	.4478
7.5	.9222	.0778	31.5	.7117	.2883	55.5	.5492	.4508
8.0	.9172	.0828	32.0	.7078	.2922	56.0	.5462	.4538
8.5	.9123	.0877	32.5	.7040	.2960	56.5	.5433	.4567
9.0	.9074	.0926	33.0	.7002	.2998	57.0	.5404	.4596
9.5	.9025	.0975	33.5	.6965	.3035	57.5	.5375	.4625
10.0	.8976	.1024	34.0	.6927	.3073	58.0	.5346	.4654
10.5	.8928	.1072	34.5	.6890	.3110	58.5	.5317	.4683
11.0	.8880	.1120	35.0	.6853	.3147	59.0	.5288	.4712
11.5	.8832	.1168	35.5	.6816	.3184	59.5	.5260	.4740
12.0	.8785	.1215	36.0	.6779	.3221	60.0	.5232	.4768
12.5	.8737	.1263	36.5	.6743	.3257	60.5	.5203	.4797
13.0	.8690	.1310	37.0	.6706	.3294	61.0	.5175	.4825
13.5	.8644	.1356	37.5	.6670	.3330	61.5	.5148	.4852
14.0	.8597	.1403	38.0	.6634	.3366	62.0	.5120	.4880
14.5	.8551	.1449	38.5	.6599	.3401	62.5	.5092	.4908
15.0	.8505	.1495	39.0	.6563	.3437	63.0	.5065	.4935
15.5	.8459	.1541	39.5	.6528	.3472	63.5	.5038	.4962
16.0	.8413	.1587	40.0	.6493	.3507	64.0	.5010	.4990
16.5	.8368	.1632	40.5	.6458	.3542	64.5	.4983	.5017
17.0	.8323	.1677	41.0	.6423	.3577	65.0	.4957	.5043
17.5	.8278	.1722	41.5	.6388	.3612	65.5	.4930	.5070
18.0	.8234	.1766	42.0	.6354	.3646	66.0	.4903	.5097
18.5	.8189	.1811	42.5	.6320	.3680	66.5	.4877	.5123
19.0	.8145	.1855	43.0	.6286	.3714	67.0	.4851	.5149
19.5	.8101	.1899	43.5	.6252	.3748	67.5	.4825	.5175
20.0	.8058	.1942	44.0	.6219	.3781	68.0	.4799	.5201
20.5	.8014	.1986	44.5	.6185	.3815	68.5	.4773	.5227
21.0	.7971	.2029	45.0	.6151	.3849	69.0	.4747	.5253
21.5	.7928	.2072	45.5	.6118	.3882	69.5	.4722	.5278
22.0	.7885	.2115	46.0	.6085	.3915	70.0	.4696	.5304
22.5	.7843	.2157	46.5	.6053	.3947	70.5	.4671	.5329
23.0	.7801	.2199	47.0	.6020	.3980	71.0	.4646	.5354
23.5	.7759	.2241	47.5	.5988	.4012	71.5	.4621	.5379

Y-90 Ingrowth Factors (0-27 Days)

t (days)	$1-e^{-\lambda t}$	t (days)	$1-3^{-\lambda t}$	t (days)	$1-e^{-\lambda t}$
0.00	.0000	9.00	.9029	18.00	.9906
0.25	.0627	9.25	.9090	18.25	.9912
0.50	.1215	9.50	.9147	18.50	.9917
0.75	.1766	9.75	.9201	18.75	.9922
1.00	.2283	10.00	.9251	19.00	.9927
1.25	.2767	10.25	.9298	19.25	.9932
1.50	.3221	10.50	.9342	19.50	.9936
1.75	.3646	10.75	.9384	19.75	.9940
2.00	.4045	11.00	.9422	20.00	.9944
2.25	.4418	11.25	.9458	20.25	.9948
2.50	.4768	11.50	.9492	20.50	.9951
2.75	.5097	11.75	.9524	20.75	.9954
3.00	.5404	12.00	.9554	21.00	.9957
3.25	.5692	12.25	.9582	21.25	.9959
3.50	.5963	12.50	.9608	21.50	.9962
3.75	.6216	12.75	.9633	21.75	.9964
4.00	.6453	13.00	.9656	22.00	.9967
4.25	.6676	13.25	.9678	22.25	.9969
4.50	.6884	13.50	.9697	22.50	.9971
4.75	.7080	13.75	.9716	22.75	.9973
5.00	.7263	14.00	.9734	23.00	.9974
5.25	.7435	14.25	.9751	23.25	.9976
5.50	.7596	14.50	.9766	23.50	.9977
5.75	.7746	14.75	.9781	23.75	.9979
6.00	.7888	15.00	.9795	24.00	.9980
6.25	.8020	15.25	.9808	24.25	.9981
6.50	.8145	15.50	.9820	24.50	.9982
6.75	.8261	15.75	.9831	24.75	.9984
7.00	.8370	16.00	.9842	25.00	.9985
7.25	.8472	16.25	.9852	25.25	.9986
7.50	.8568	16.50	.9861	25.50	.9987
7.75	.8658	16.75	.9870	25.75	.9987
8.00	.8742	17.00	.9878	26.00	.9988
8.25	.8820	17.25	.9886	26.25	.9989
8.50	.8896	17.50	.9893	26.50	.9990
8.75	.8964	17.75	.9900	26.75	.9990
				27.00	.9991

Sr-89 Decay Factors (0-59.5 Days)

(t 1/2 = 51 days)

t (days)	$e^{-\lambda t}$	t (days)	$e^{-\lambda t}$	t (days)	$e^{-\lambda t}$
0.0	1.0000	20.0	.7620	40.0	.5808
0.5	.9932	20.5	.7569	40.5	.5769
1.0	.9865	21.0	.7518	41.0	.5730
1.5	.9798	21.5	.7568	41.5	.5690
2.0	.9732	22.0	.7416	42.0	.5652
2.5	.9668	22.5	.7366	42.5	.5613
3.0	.9601	23.0	.7317	43.0	.5575
3.5	.9536	23.5	.7267	43.5	.5539
4.0	.9471	24.0	.7218	44.0	.5500
4.5	.9407	24.5	.7169	44.5	.5462
5.0	.9344	25.0	.7120	45.0	.5427
5.5	.9280	25.5	.7072	45.5	.5380
6.0	.9217	26.0	.7023	46.0	.5352
6.5	.9155	26.5	.6977	46.5	.5318
7.0	.9093	27.0	.6930	47.0	.5280
7.5	.9031	27.5	.6882	47.5	.5245
8.0	.8970	28.0	.6836	48.0	.5210
8.5	.8909	28.5	.6790	48.5	.5175
9.0	.8849	29.0	.6742	49.0	.5140
9.5	.8789	29.5	.6699	49.5	.5105
10.0	.8729	30.0	.6651	50.0	.5070
10.5	.8670	30.5	.6608	50.5	.5035
11.0	.8612	31.0	.6562	51.0	.5000
11.5	.8553	31.5	.6519	51.5	.4967
12.0	.8495	32.0	.6473	52.0	.4933
12.5	.8438	32.5	.6430	52.5	.4900
13.0	.8381	33.0	.6388	53.0	.4868
13.5	.8324	33.5	.6342	53.5	.4834
14.0	.8268	34.0	.6300	54.0	.4801
14.5	.8212	34.5	.6259	54.5	.4769
15.0	.8156	35.0	.6215	55.0	.4734
15.5	.8101	35.5	.6172	55.5	.4702
16.0	.8046	36.0	.6131	56.0	.4671
16.5	.7992	36.5	.6090	56.5	.4640
17.0	.7938	37.0	.6050	57.0	.4608
17.5	.7883	37.5	.6009	57.5	.4578
18.0	.7881	38.0	.5968	58.0	.4547
18.5	.7778	38.5	.5928	58.5	.4513
19.0	.7725	39.0	.5888	59.0	.4484
19.5	.7672	39.5	.5848	59.5	.4454

STRONTIUM - 90

λ factor = 0.0062559 (0.25)

$T_{\frac{1}{2}} = 27.7 \text{ y}$

Months Years	0	3	6	9	12	15	18	21	24	27	30	33
0	1.0000	.9937	.9876	.9814	.9753	.9692	.9631	.9572	.9512	.9452	.9394	.9335
3	.9277	.9219	.9161	.9104	.9047	.8991	.8935	.8879	.8824	.8769	.8714	.8660
6	.8606	.8552	.8499	.8446	.8393	.8341	.8289	.8237	.8186	.8135	.8084	.8033
9	.7983	.7934	.7884	.7835	.7786	.7737	.7689	.7641	.7594	.7546	.7499	.7452
12	.7406	.7360	.7314	.7268	.7223	.7178	.7133	.7089	.7044	.7000	.6957	.6913
15	.6870	.6827	.6785	.6742	.6701	.6659	.6617	.6576	.6535	.6494	.6454	.6413
18	.6373	.6334	.6294	.6255	.6216	.6177	.6139	.6100	.6062	.6024	.5987	.5949
21	.5912	.5875	.5839	.5802	.5766	.5730	.5695	.5659	.5624	.5589	.5554	.5519
24	.5485	.5451	.5417	.5383	.5349	.5316	.5283	.5250	.5217	.5184	.5152	.5120
27	.5088	.5056	.5025	.4993	.4962	.4931	.4901	.4870	.4840	.4809	.4780	.4750
30	.4720	.4691	.4661	.4632	.4603	.4575	.4546	.4518	.4489	.4462	.4434	.4406
33	.4379	.4351	.4324	.4297	.4270	.4244	.4217	.4191	.4165	.4139	.4113	.4088
36	.4062	.4037	.4011	.3986	.3961	.3937	.3912	.3888	.3864	.3840	.3816	.3792
39	.3768	.3745	.3721	.3698	.3675	.3652	.3629	.3607	.3584	.3562	.3540	.3518
42	.3496	.3474	.3452	.3431	.3409	.3388	.3367	.3346	.3325	.3304	.3284	.3263
45	.3243	.3223	.3202	.3183	.3163	.3143	.3123	.3104	.3084	.3065	.3046	.3027
48	.3008	.2989	.2971	.2952	.2934	.2916	.2897	.2879	.2861	.2844	.2826	.2808
51	.2791	.2773	.2756	.2739	.2722	.2705	.2688	.2671	.2654	.2638	.2621	.2605
54	.2589	.2573	.2557	.2541	.2525	.2509	.2493	.2478	.2462	.2447	.2432	.2417
57	.2402	.2387	.2372	.2357	.2342	.2328	.2313	.2299	.2284	.2270	.2256	.2242
60	.2228	.2214	.2200	.2186	.2173	.2159	.2146	.2132	.2119	.2106	.2093	.2080
63	.2067	.2054	.2041	.2028	.2016	.2003	.1991	.1978	.1966	.1954	.1941	.1929
66	.1917											

CHEMICAL COMPOSITION OF COWS' MILK

Ranges are given in parentheses, and represent estimate "c" of the
95 o/o range (cf introduction).

Constituent per 100 ml Whole Milk	Cow Mature Milk
Calcium, mg	125 (56-381)
Chlorine, mg	103 (70-290)
Cobalt, µg	0.06
Copper, mg	0.03 (0.003-0.40)
Fluorine, µg	16 (7-28)
Iodine, µg	21 (0.4-187)
Iron, mg	0.10 (0.01-1.0)
Magnesium, mg	12 (7-22)
Manganese, µg	2 (<1-4)
Phosphorus, mg	96 (560129)
Potassium, mg	138 (38-287)
Silicon	Trace
Sodium, mg	58 (31-214)
Sulfur, mg	30 (24-44)
Zinc, mg	0.38 (0.17-0.66)