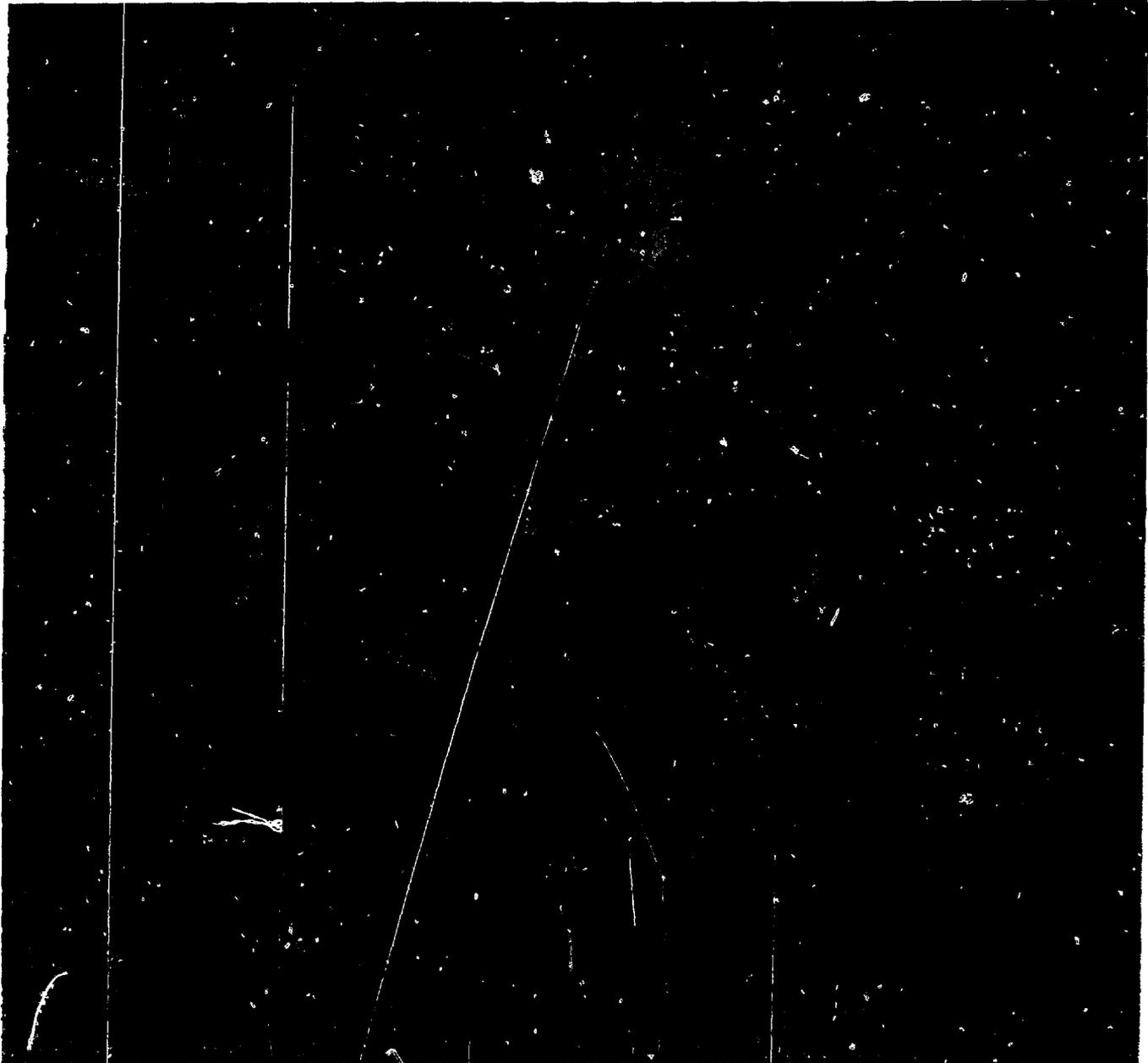


**The Determination of Environmental Levels of
Uranium and Thorium Series Isotopes and ^{137}Cs
in Aquatic and Terrestrial Samples**

P. Wilkinson

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ABSTRACT

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This publication details the analytical methods used at the Freshwater Institute for the radiochemical analysis of aquatic and terrestrial samples. Sample collection methods are described with emphasis on water sampling. A detailed "Calculations" section contains the mathematical formulae used to determine the absolute activity of each isotope analyzed.

RÉSUMÉ

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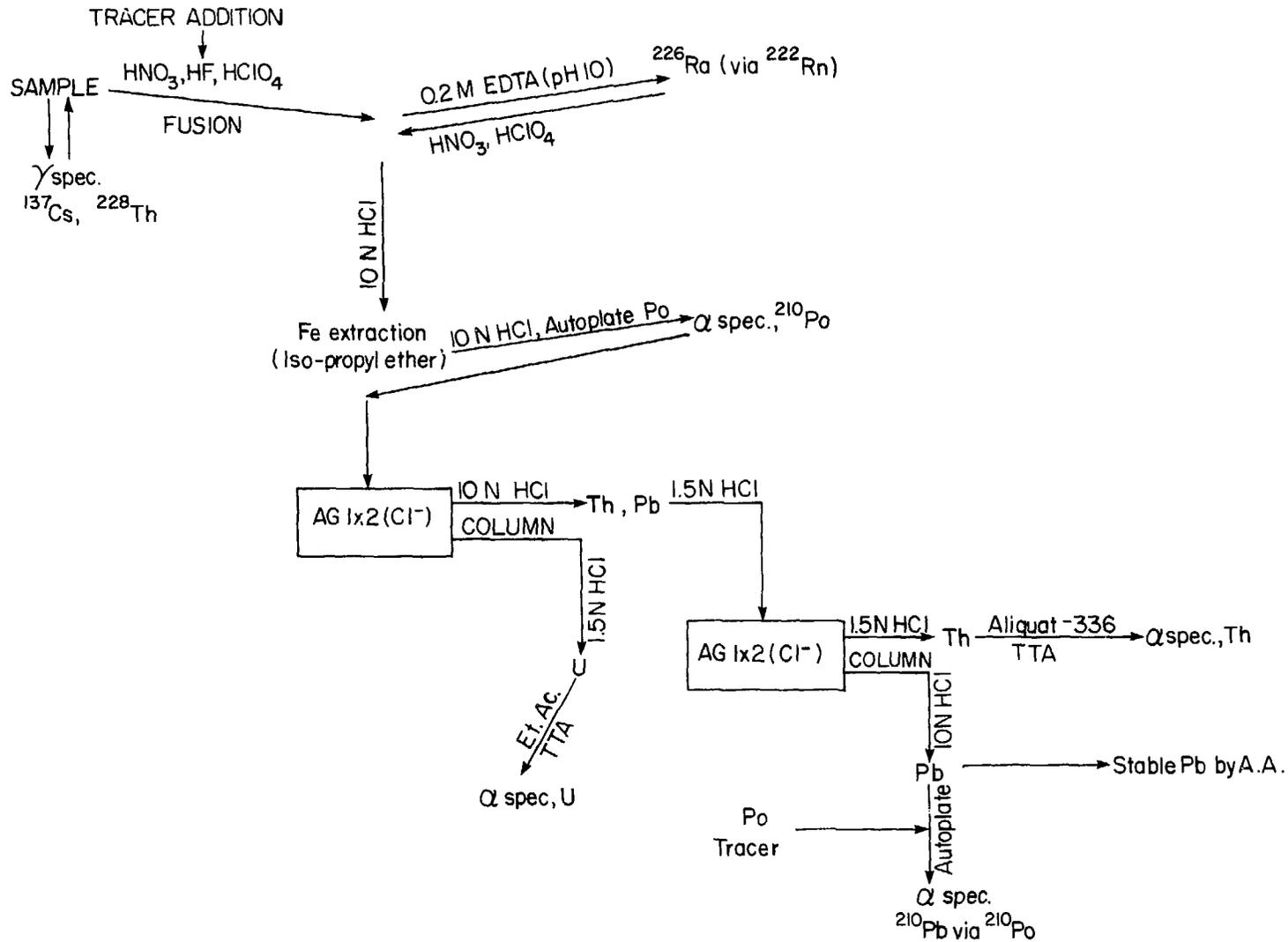
Le présent document expose en détails les méthodes analytiques utilisées à l'Institut des eaux douces pour l'analyse radiochimique d'échantillons d'eau et de sol. Il décrit les méthodes de collecte d'échantillons, en particulier les échantillons d'eau. Une section détaillée de calculs porte sur les formules mathématiques utilisées pour déterminer l'activité absolue de chaque isotope analysé.

INTRODUCTION

The use and measurement of radioisotopes in the environment can be a powerful tool in limnological research. Scientists at the Freshwater Institute have utilized radioisotopes as tracers in lake studies to determine lake mixing rates (Quay et al. 1979), gas diffusion (Hesslein et al. 1979), and pathways and movement rates of heavy metals in whole lake systems (Hesslein et al. 1980; Hesslein and Slavicek 1984). Research programs are also underway to develop models of the seasonal cycles of natural uranium and thorium series isotopes in freshwater lake systems and to determine uranium and thorium series nuclides in freshwater and estuarine food chains. These latter programs require a wide variety of samples to be taken (water, soils, sediments, plants, and animals) and each is analyzed for alpha and gamma emitting isotopes (U and Th isotopes, ^{210}Po , ^{210}Pb and ^{137}Cs). Lead-210 and ^{137}Cs are also used as a radiochemical tool to determine lake sedimentation rates (Robbins 1978; Robbins and Edgington 1975).

This manual describes the sample collection methods and analytical procedures used at the Freshwater Institute to determine the amounts of U and Th series isotopes and bomb-fallout ^{137}Cs in aquatic and terrestrial environmental samples. It is assumed that the reader is familiar with the principles of radiochemistry and radiation detection. An excellent introduction to radiochemical fundamentals can be found in a radiochemical procedures manual by Smithson et al. (1978) and mandatory reading for any radiochemist is the text by Friedlander et al. (1981).

Fig1: ANALYTICAL FLOW DIAGRAM FOR U AND Th SERIES ISOTOPES



METHODS PRINCIPLE

Figure 1 shows the order in which the sequential analysis proceeds. Prior to any acid digestion the sample is counted on a germanium lithium (Ge(Li)) detector to obtain a gamma energy spectrum. The ^{137}Cs and ^{228}Th activities are determined by comparing the counts obtained in the 662 KeV and 239 KeV lines of ^{137}mBa and ^{212}Pb respectively with those obtained from counting a National Bureau of Standards (NBS) sample certified for ^{137}Cs and ^{228}Th and having the same geometry.

The next step involves the decomposition of refractory organic and inorganic compounds by dry ashing at 400°C and/or digestion with strong acids. Sediment and soil samples also undergo a low temperature pyrosulfate fusion (Sill and Willis 1977) in order to further break down refractory compounds, particularly tri- and quadri-valent compounds. Also, isotopic tracers of known activity are added to determine the yields and the absolute activities of the isotopes to be measured. The tracers are added as early in the decomposition step as possible to ensure that homogeneity is reached with the isotopes in the sample. As there is no suitable isotopic tracer for ^{210}Pb , stable lead is used.

Radium-226 is determined by measuring the activity of its gaseous daughter, ^{222}Rn , when the state of equilibrium between the two is known. The particular method of separating and isolating ^{222}Rn used here was first described by Broecker (1965) and Mathieu (1977). The analysis is carried out with the sample in 0.15 M EDTA at pH ≈ 10.0 to ensure that ^{226}Ra remains in solution and is not precipitated as sulfate or coprecipitated with other cations. Some samples, when dissolved in 8 N HCl, exhibit an apparent decrease in ^{226}Ra activity when repeated emanations of ^{222}Rn were carried out on the same sample over a period of several weeks. This effect was not

observed with samples collected on manganese impregnated acrylic fibers that were analyzed after leaching in 6 N HCl.

The absolute activities of uranium and thorium isotopes and ^{210}Po are determined from the alpha energy spectrum recorded by a silicon surface barrier detector by comparing the integral of the isotope peak with that of the isotope tracer peak of known activity. The polonium counting disc is prepared by the spontaneous deposition of polonium onto a silver disc (Figgins 1961; Flynn 1968) from 10 N HCl at 80°C. Because the ferric ion inhibits the migration of polonium, it is extracted with iso-propyl ether (Nielson 1960) before autodeposition. Uranium, thorium and lead are separated on a strong base anion exchange resin in the chloride form (Rieman and Walton 1970). Uranium is strongly absorbed on the column in 10 N HCl, lead is absorbed in 1.5 N HCl, and thorium is not absorbed in any normality of HCl. By proper control of acid strength, separation is achieved, sequentially, using the same column. Thorium is further purified by extraction from acidic aluminum nitrate solution into Aliquat 336 (Sill et al. 1974) and stripping into 10 N HCl. Uranium is purified by extraction from nitrate solution into ethyl acetate and back extraction into water (Gindler 1962). The uranium and thorium counting discs are prepared by extracting each from aqueous solution at pH 4 and 2, respectively into 0.2 M TTA (thenoyltrifluoroacetone) and evaporating the TTA onto stainless steel discs. As polonium is strongly absorbed on the ion exchange column in all HCl strengths, the separated lead portion is free of polonium. The lead yield is determined by atomic adsorption analysis. The ^{210}Pb activity is determined by analyzing the lead portion for ^{210}Po that grows in over a known period of time.

REAGENTS

1. Water Sampling

Acids: A.C.S. Reagent Grade conc. HCl

Base: 10 N NaOH

AMP: Ammonium molybdophosphate (BioRad, Mississauga, Ont.)

Ferric Chloride Solution: 75% w/w (Fisher Sci. #SO-F-102)

Manganese impregnated acrylic fibers: Heat the acrylic fiber (Monsanto's Acrilan, 3.0 denier, type B-16) in one fiber volume of 0.5 M KMnO_4 for 10 min at 75°C. Remove the fiber and wash thoroughly with (d) H_2O .

2. Analytical

(i) Acids (A.C.S. reagent grade conc. HCl, HNO_3 , H_2SO_4 , HF (48%), HClO_4 (70-72%))

(ii) 10 N NaOH: Add 400 g NaOH slowly with vigorous stirring to 500 mL (d) H_2O

1.5 N HCl: Add 125 mL conc. HCl to 875 mL (d) H_2O

10 N HCl: Add 833 mL conc. HCl to 167 mL (d) H_2O

8 N HNO_3 : Add 500 mL of conc. HNO_3 to 500 mL (d) H_2O

4 N HNO_3 : Add 250 mL of conc. HNO_3 to 750 mL (d) H_2O in a 2 L plastic beaker. Cool and dilute to approximately 1 L. Store in a polypropylene bottle.

(iii) ITA (Thengyltrifluoroacetone): Dissolve 5.6 g ITA in 100 mL benzene.

(iv) 0.15 M EDTA: Dissolve 30 g NaOH in ≈ 300 mL of (d) H_2O in a 2 L beaker. Add 56 g EDTA and stir until dissolved. Dilute to 1 L and adjust to pH 10 using 10 N NaOH.

- (v) Aliquat 336 (General Mills Inc., Kankakee, IL): Dissolve 300 mL of Aliquat 336 in 700 mL of Xylenes in a 2 L separatory funnel. Wash twice with each of 4 N HNO₃ and (d)H₂O. Discard washes and store organic phase in a 1 L glass reagent bottle.
- (vi) Aluminum Nitrate (2.2 M): (for Th separation) Dissolve 825 g of Al(NO₃)₃·9H₂O in 450 mL of warm (d)H₂O. Add 85 mL of HNO₃, cool and filter through a glass fiber filter.
- (vii) Aluminum Nitrate (2 M): (for U separation) Dissolve 187.6 g of Al(NO₃)₃·9H₂O in 150 mL (d)H₂O. Dilute to 250 mL.
- (viii) Chromic/Acid Cleaning Solution: Add 140 g of K₂Cr₂O₇ to a 9 lb bottle of conc. H₂SO₄. Invert several times to mix. Do not discard the solid K₂Cr₂O₇ which does not dissolve.
- (ix) Ion-Exchange Resin: Bio-Rad, AG 1x2, 100-200 mesh, Cl⁻ form.

APPARATUS

1. Water sampling

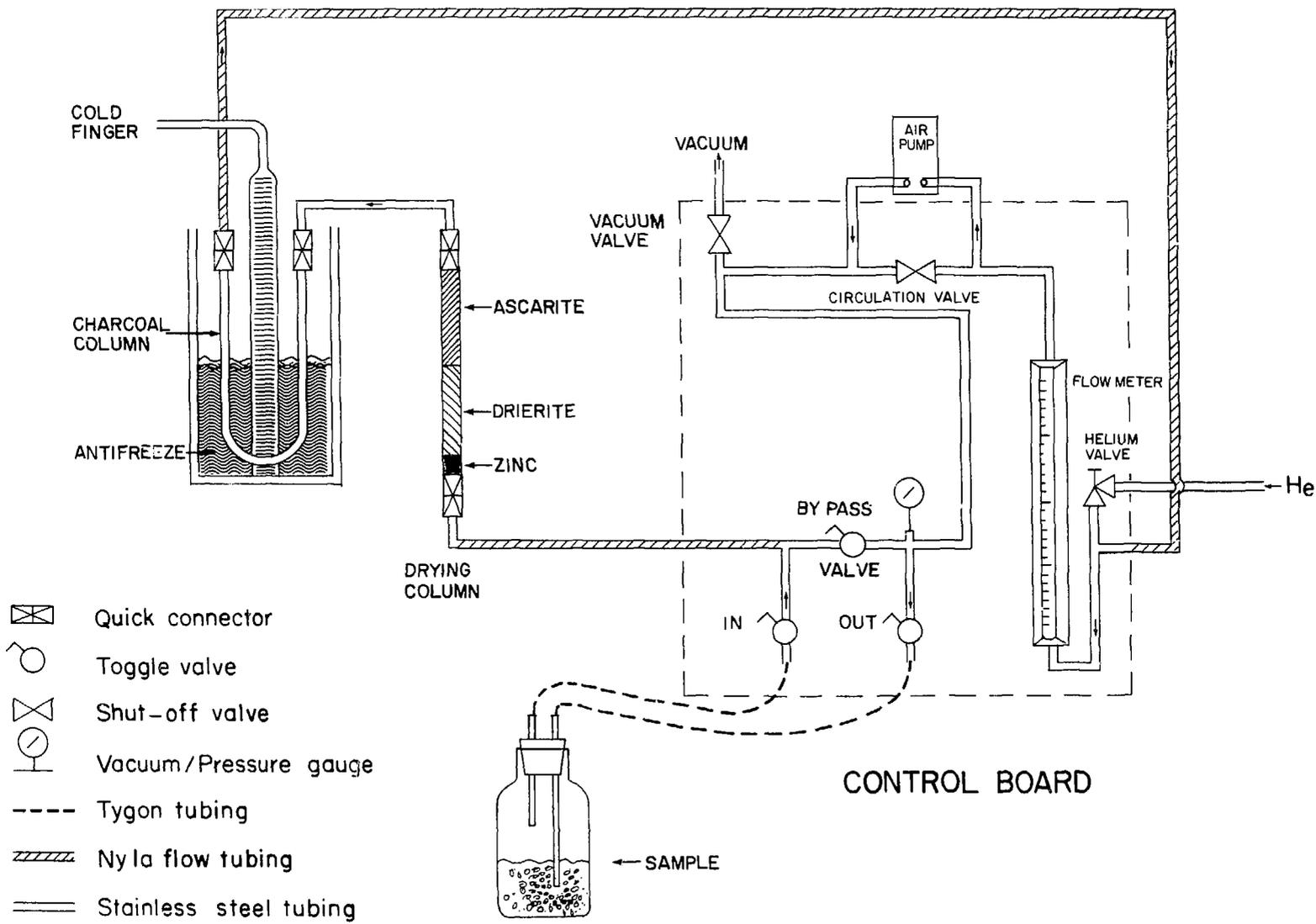
- 1) Sample container: 60 L capacity Deldrum (Container Corp. of America, Wilmington, DE)
- 2) Water pump: Monarch PBGF-6 corrosion resistant, self-priming, gasoline engine pump or equivalent
- 3) Pump fittings: 13 mm dia rubber garden hose
38 mm dia swimming pool vacuum hose
assorted hose clamps and connectors
- 4) Filter apparatus: (1) Millipore 142 mm PVC filter holder
(Cat #4440 142 00) and 142 mm MF-Millipore filters
or (2) Millipore Pelicon Cassette System
(Cat # XX42 ASY 60) and filter cassette
(Cat #HVLP 000CS)
- 5) 210 L. drum: ≈57 cm dia x 85 cm ht. with one end open
- 6) Plastic barrel liners: Winliner (Hedwin Corp., N.Y., NY)
(0.1 mm thick x 94 cm dia x 142 cm long)
- 7) Drum stirrer: Canoe paddle
- 8) Siphon tubes: various lengths of 13 mm and 6.4 mm dia. copper and tygon tubing
- 9) Cubitainers: 4 L capacity (Hedwin Corp. N.Y., NY)
- 10) pH test papers: "Color pHast" (Sargent-Welch #S-65271)

2. Analytical

1. Beakers: Teflon (FEP) and glass in assorted sizes (50-4000 mL).
2. Erlenmeyers: Glass, assorted sizes (125-250 mL).
3. Glass watch glasses (50-150 mm. dia.).

4. Ceramic and asbestos pads (15 x 15 cm).
5. Hot-plate/stirrers.
6. Distillation apparatus for ether distillation and blubber digestion
7. Fumehoods: Perchloric and stainless steel lined, both with venturi washdown.
8. Separatory funnels (250 and 500 mL).
9. Ion exchange columns (35 x 2.5 cm).
10. Vibro-Graver (Fisher Sci. #13-389-10).
11. Filtering apparatus (Millipore, XX10 047 00).
12. Eppendorf pipettes (50-1000 μ L).
13. Graduated cylinders (50-1000 mL).
14. Disposable pipettes and test tubes.
15. Analytical balance.
16. Counting discs. Silver (Johnson Matthey Ltd., Toronto) and stainless steel (Metallic Valve Co. Ltd., Birkenhead, U.K.).
17. Disposable plastic petri dishes (Falcon, 50 x 9 mm)
18. Radium-226 counting equipment consisting of radon extraction board (Fig. 2). Radon transfer board (Fig. 3), scintillation counting cells (Applied Science of Piermont, Piermont, NY), scintillation counter (Applied Techniques Co., Monroe, NY), cold finger (Neslab, Portsmouth, NH) and a vacuum pump.
19. Alpha spectroscopy system consisting of Ortec model 576 dual alpha spectrometers c/w surface barrier detectors, NIM power supply, mixer router, multichannel analyzer and vacuum pump.
20. Gamma spectroscopy system consisting of a lithium drifted germanium detector, NIM power supply, detector bias supply, preamp and spectroscopy amplifier, multichannel analyzer and automatic sample changer.

Fig 2: RADON EXTRACTION BOARD



-  Quick connector
-  Toggle valve
-  Shut-off valve
-  Vacuum/Pressure gauge
-  Tygon tubing
-  Nyla flow tubing
-  Stainless steel tubing

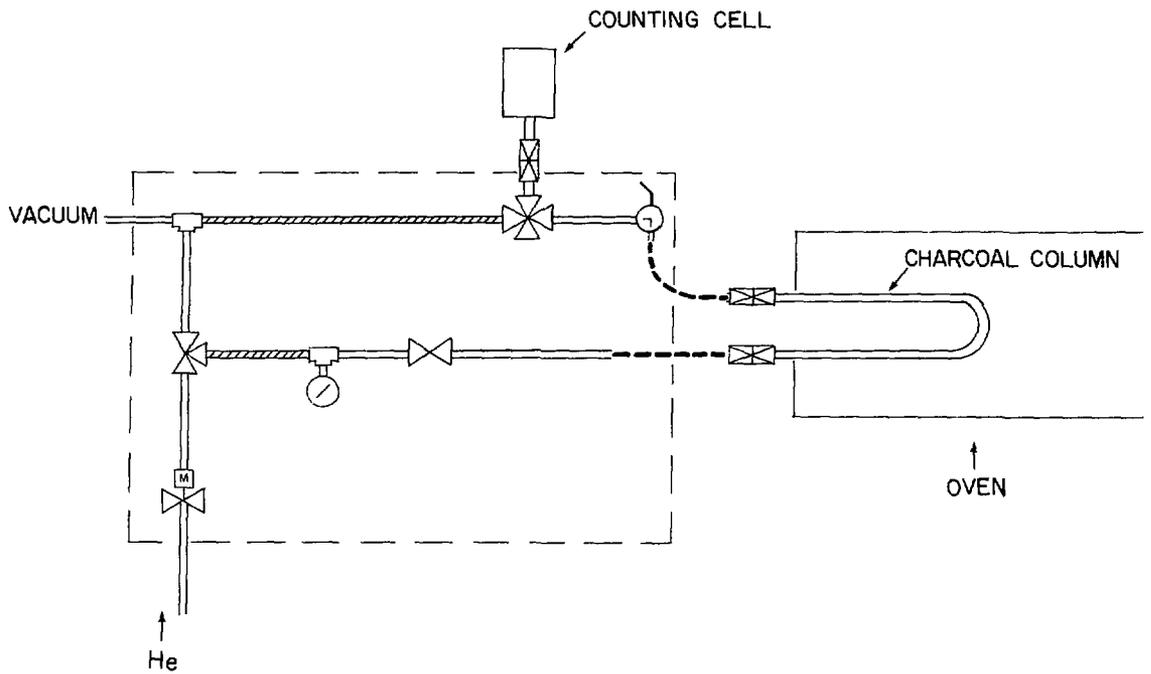


Fig 3 : RADON TRANSFER BOARD

- | | | | |
|---|-----------------------|---|------------------------|
|  | Vacuum/Pressure gauge |  | Tygon tubing |
|  | Metering valve |  | Toggle valve |
|  | 3-Way valve |  | Stainless steel tubing |
|  | Shut-off valve |  | Nyla flow tubing |
|  | 4-Way valve | | |
|  | Quick connector | | |

RADIOISOTOPE TRACERS AND STANDARDIZATION

The radioisotope tracers identified in Table 1 are used to determine the absolute activities of the isotopes of interest and are standardized by the methods indicated. The tracer solutions should be standardized by weight rather than volume (i.e. Bq·g⁻¹) to allow for more precise additions using eppendorf pipettes which can be calibrated to deliver a known weight of each tracer solution. The amount of tracer added varies with the sample size and the suspected activity of the isotope to be measured. Care must be taken with the amount of tracer added to avoid any interference to neighboring lower alpha energy peaks or from higher alpha energy peaks.

Table 1. Radioisotope tracers (Lederer and Shirley 1978).

Tracer isotope	Half life	Decay mode detected	Energy (MeV) and intensity of radiation	Method of standardization
U-236	2.34 x 10 ⁷ yr	alpha	4.49(74%), 4.33 (26%)	a
U-232	71.7 yr	alpha	5.32(68%), 5.27(32%)	a
Th-229	7340 yr	alpha	5.05(7%), 4.97(10%) 4.90(11%), 4.84(58%) 4.81(11%)	b
Th-228	1.91 yr	alpha	5.43(71%), 5.34(28%)	b,c
Po-209	102 yr	alpha	4.88(99%)	d,e
Po-208	2.90 yr	alpha	5.11(99%)	d,e
Cs-134	2.06 yr	gamma	0.57(23%, complex) 0.605(98%), 0.796(99%)	f

- a) Measured amounts of tracer and ^{238}U standard (NBS 960) are mixed together, plated as described in the analytical section and counted on the alpha spectrometer.
- b) Measured amounts of tracer and ^{230}Th standard (U.S. EPA) are mixed together, plated as described in the analytical section and counted on an alpha spectrometer.
- c) A measured amount of tracer is placed on a glass fiber filter in a plastic petri dish, sealed and gamma counted using a GeLi detector. The 239 KeV line of ^{212}Pb is compared with that of a standard ^{228}Th (Amersham, RLZ.44) source of similar geometry.
- d) A 50 μL aliquot is evaporated on a stainless steel disc and counted on an alpha spectrometer. The counting efficiency is determined by counting a standard ^{226}Ra (NBS 4953C) disc having the same geometry.
- e) Measured amounts of tracer and ^{210}Po standard (Amersham, PDZ.42) are mixed together, plated as described in the analytical section, and counted on an alpha spectrometer.
- f) Standard ^{134}Cs (Amersham, CCZ.72) diluted to an exact volume.

SAMPLE COLLECTION

Samples are collected in the field by personnel manning permanent or seasonal field camps or by the researchers themselves during periodic sampling excursions to sometimes remote locations. In some cases, the cooperation and help of the local population is sought as is the case for obtaining samples of arctic marine mammals from Inuit hunters. Collection techniques include sample gathering by hand for plants and soil samples and the use of collection aids such as nets to sample fish, phytoplankton, and zooplankton. Mechanical collection devices such as the Ekman dredge (Flannagan 1970) and the K-B Corer (Brinkhurst et al. 1969) are used to sample lake sediments in bulk and to obtain sediment cores. The use of divers to take dredge samples and sediment cores by hand provides a better sample than when mechanical collectors are lowered from boats and the penetration depth is difficult to control.

Two hundred litre samples of lake water have been filtered using two types of apparatus. The first is a Millipore 142 mm dia. filter holder using a 1.2 μm MF-Millipore filter. The holder is connected to the pump and water is pumped through the filter at 15-20 psi until the flow stops or slows to a trickle indicating that the filter is plugged and must be replaced. The filters are collected and saved for analysis. An average of 30-50 filter changes are necessary per sample and the average time required is 5 hours. When 0.45 μm filters are used, the number of filter changes and time required more than doubles.

The Millipore Pelicon Cassette System employs a tangential flow process across the membrane surface which keeps the solids in suspension and thus avoids clogging of the filter and the need to replace it. For filtering lake water samples the Millipore Durapore Cassette (0.5 μm , 1500 mm^2) is used. Water is pumped through the Cassette System at a back pressure of 10-15 psi

producing a filtered flow of 3-5 L·min⁻¹. If the suspended solids are to be retained, a recirculation loop is used whereby the solids-liquid flow is returned to the original unfiltered sample reservoir until approximately 1-2 L volume remains. This "concentrate" can be transported to the lab for collection of solids by centrifugation.

The sampling of filtered and unfiltered water is carried out by two methods. The first involves the collection of a 60 L volume in a Deldrum (T.M.: Container Corp. of America, Wilmington, DE) which is a sturdy, black plastic barrel that can be filled by direct immersion or using a pail or pump and shipped back to the lab for analysis. The second method involves the concentration of the isotopes from a large volume water sample to a smaller sample using chemical and physical methods.

Radium is collected by adsorption onto manganese impregnated acrylic fibers (Moore and Reid 1973; Moore 1976). The water sample in a container of known volume is siphoned (150-250 mL·min⁻¹) through a 50 mL syringe packed with manganese impregnated acrylic fiber. The used fiber is transported to the lab sealed in a whirl pac to avoid drying and subsequent loss of manganese oxides.

Cesium is adsorbed onto the cation exchange resin: ammonium molybdophosphate (AMP) (Feldman and Rains 1964) at low pH. The water is pumped from the sample source into a 210 L drum which is double-lined with disposable barrel liners. The sample is acidified (pH 1.5) and the added analytical tracer, ¹³⁴Cs, is allowed to equilibrate for at least 1 hour before 20 g of AMP is added and thoroughly mixed. When the AMP settles to the bottom, the slurry is poured into plastic "cubitainers" and transported to the lab for analysis.

Uranium, thorium, polonium, and lead are precipitated from the water sample as hydroxides and collected on an iron-hydroxide floc. Added

analytical tracers (^{232}U , ^{228}Th , ^{209}Po and stable lead) are allowed to equilibrate for at least 1 hour with the acidified (pH 1.5) water sample contained in a 210 L plastic lined drum. After mixing in 2 g of Fe^{3+} (as FeCl_3 solution) the pH is increased to 9-10 with NaOH and as large as possible flocs are formed by gentle stirring of the sample. When the floc has settled to the bottom, the supernatant water is siphoned off and the flocculant precipitate is poured into a cubitainer and transported to the lab for analysis.

SAMPLE PREPARATION

1. Soils and Sediments

Soils, sediment cores, dredge samples, etc. must be dried either in the oven or freeze drier to determine % water. Record wet weight of sample, oven dry or freeze dry, and record dry weight. Weigh as much sample as possible into a plastic petri dish for γ analysis of ^{137}Cs and ^{212}Po . Record on the dish cover, the sample number, weight and date sealed.

Dissolution: Weigh 1-3 g of sample into a 150 mL teflon (FEP) beaker. Slowly add 10 mL of conc. HNO_3 to digest the most reactive organics and swirl gently until any reaction ceases. Using an eppendorf pipette, add the U, Th, Po, and stable Pb tracers. Add 20 mL of HF to volatilize any silica present in the sample, 5 mL of HClO_4 to digest any remaining organics and heat to dryness on a hot plate. Any remaining HF is removed with the fumes of HClO_4 . Ensure that an asbestos pad and a ceramic pad are between the teflon beaker and the hot-plate and adjust the temperature so that the beaker does not melt or stick to the ceramic pad.

Add 15 mL of conc. H_2SO_4 and heat to fumes of H_2SO_4 . When the solution no longer wets the sides of the beaker and rolls around the bottom like a pool of mercury, quantitatively transfer it to a 250 mL erlenmeyer flask containing 3 g of anhydrous Na_2SO_4 . Immediately evaporate the sample over a blast burner to get rid of any remaining HF and thus avoid the reintroduction of silica to the sample. Heat to a pyrosulfate fusion as indicated by the formation of a clear melt and no fumes. Cool on an asbestos pad and proceed as under "Analytical" for ^{226}Ra or ^{210}Po .

2. Biological Samples

This section is intended to cover whole samples and specific dissected parts excluding blubber but including bone, flesh, shell, organs, etc. for fresh and salt water: fish, crabs, mussels, oysters, seal, walrus, bear, birds, etc.

It is extremely important that all biological information be determined and recorded for each sample prior to any sample preparation steps being taken. This information includes taxonomy, sex, weight, and physical dimensions as well as sample location and date. For some samples it is necessary to take a sample for age determination, i.e. otoliths from fish and an eye and a tooth from seals.

Dissolution: Cut the sample into small cubes ($\approx 2 \text{ cm}^3$), place in a weighed 600 mL beaker, and determine the wet weight. Dry the sample at 110°C in a vented oven and determine dry weight. Add approximately 20 mL of conc. HNO_3 , cover with a watch glass, and heat on a hot plate. Add additional nitric acid when the reaction ceases or the contents of the beaker approach dryness. Special care must be taken to avoid any sample loss during this period when the sample is not spiked with tracers. Applied heat must be regulated to avoid excessive reaction in some samples with high fat content. It is advisable to have a cooling bath on hand which can be used to slow down an overly rigorous digestion.

Digest the sample until it appears soluble in the acid. Using an eppendorf pipette, add the U, Th, Po, and stable Pb tracers and continue heating for at least 1 hour to ensure homogeneity is reached between the

tracers and isotopes to be analyzed. Remove the cover from the beaker and evaporate to dryness ensuring that sample loss due to splattering does not occur by proper regulation of temperature near dryness. Muffle the beaker and contents overnight at 400°C and weigh the cooled beaker and contents to determine ash weight. Grind the sample in the beaker and weigh as much as possible into a plastic petri dish, seal, and count on the Ge(Li) detector. When the gamma analysis is complete, return the contents to the original beaker and proceed as under "Analytical" for ^{226}Ra or ^{210}Po .

3. Blubber

This procedure is to be used for blubber samples from seal, walrus, and whale and any other high fat samples that due to their extreme reactivity, cannot be processed as described in the section: Biological Samples.

When conc. HNO_3 is added to a blubber sample, no immediate reaction occurs. With the application of heat or prolonged contact while cool, a vigorous exothermic reaction begins which, because of the extreme heat buildup, quickly results in the violent ejection of sample from the beaker unless immediate cooling is applied. In a cold bath, the reaction proceeds too slowly or not at all. The following method was developed by R.H. Hesslein and D. Fox (Freshwater Institute) to provide heat to start and maintain the reaction while at the same time providing a conductive medium to remove excess heat and prevent the reaction from becoming uncontrolled. It also provides the means for refluxing the HNO_3 and for cooling any reactive material forced out of the main sample container.

Sample size should be 100-200 g but for safety and ease of handling, 25 g subsamples are digested separately before being combined near the final steps of the procedure.

Dissolution: Cut the sample into 2 cm cubes and weigh a subsample into a 500 mL round bottom boiling flask having one center neck and one angled side neck. Connect the center neck to a reflux condenser and assemble in a water bath on a hot plate as illustrated in Fig. 4. Add ≈ 20 mL of conc. HNO_3 through the side neck and close with a glass stopper. (The stoppered side neck will act as a relief valve in case of pressure buildup.) Using an eppendorf pipette, add the U, Th, Po and stable Pb tracers. Turn on the cooling water to the column and allow the sample to sit unheated in the cold bath until any reaction subsides and it appears that the chunks of blubber

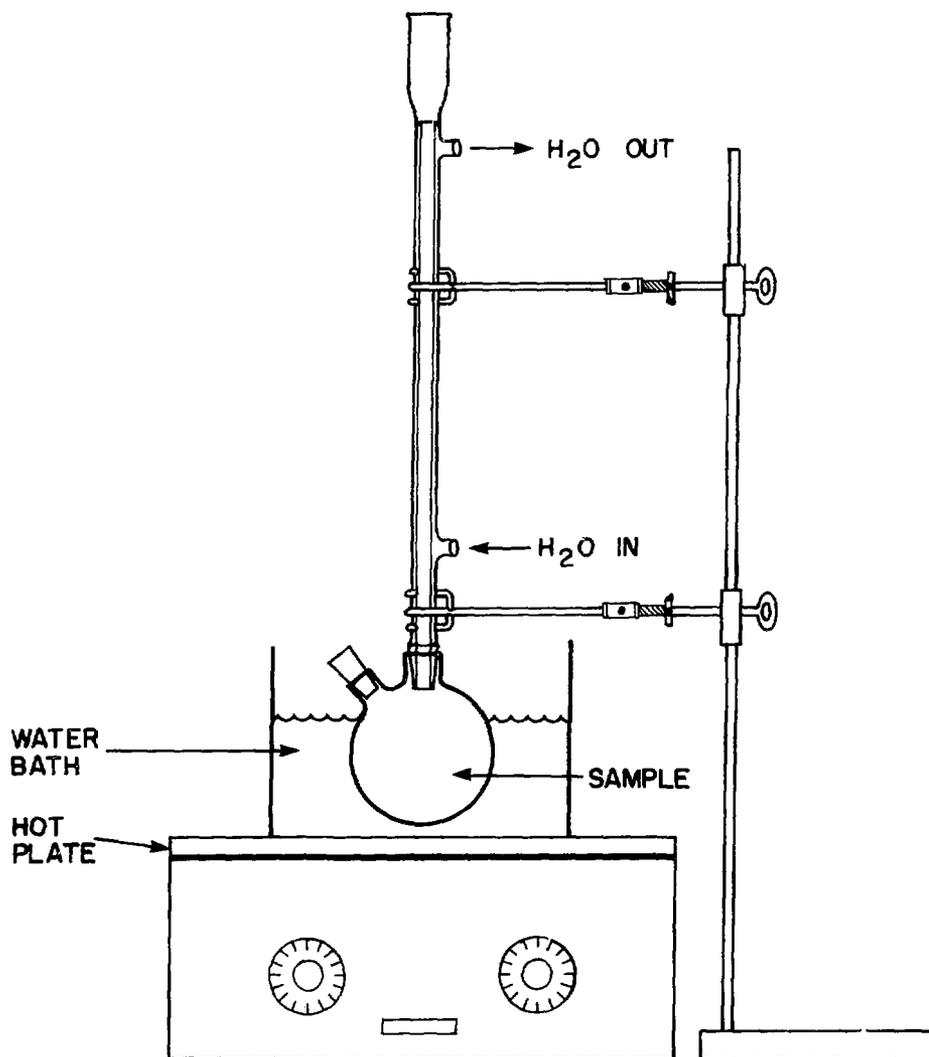


Fig 4: APPARATUS FOR DECOMPOSITION OF BLUBBER SAMPLES

have decomposed somewhat. Turn the hot plate on under the bath to obtain a water temperature of 60-80°C. Digest the sample at this temperature until the sample has liquefied. The organic layer will be cloudy and dark in color. Remove the water bath and hot plate and fit a 250 W heating mantle around the boiling flask. Starting at the low heat setting, increase the temperature stepwise, each time allowing the digestion reaction to stabilize. Continue heating until the sample becomes a clear yellow color and both organic and acid appear homogeneous. When all subsamples have been predigested and combined in a 600 mL beaker, evaporate to dryness on a hot plate. Muffle overnight at 400°C and determine the ash weight. Weigh as much as possible into a plastic petri dish, seal, and count for ^{137}Cs on the Ge(Li) detector. Replace the subsample into the original beaker and proceed as under "Analytical" for ^{226}Ra and ^{210}Po .

4. Vegetation

Wash the sample in (d)H₂O to remove any contaminating particles and air dry. Grind the sample as much as possible with a mortar and pestle or a mechanical grinder. Transfer a weighed amount of sample to a 600 mL beaker and oven dry (100°C). Record wet and dry weights. Add 30 mL of conc. HNO₃ to the beaker, cover with a watch glass and digest at low heat on a hot plate adding more acid as needed. If the sample catches fire, 8 N HNO₃ may be used instead of conc. HNO₃. When all the sample has decomposed, add the U, Th, Po and stable Pb tracers with an eppendorf pipette and heat the covered beaker on a hot plate for a least 1 hour to ensure homogeneity between sample and tracers. Remove the watch glass, evaporate to dryness with high heat, and muffle overnight at 400°C. Cool and weigh to determine ash weight. Grind the sample in the beaker and weigh as much as possible into a plastic petri dish and count for ¹³⁷Cs on the Ge(Li) detector. Recombine the contents of the petri with the remaining sample in the beaker and proceed as under "Analytical" for ²²⁶Ra or ²¹⁰Po.

5. Iron Floc

No tracers are added to these samples as they have already been added in the sampling step.

Transfer the sample to a 4 L beaker and allow the iron floc to settle. Using a copper or glass U-tube, siphon off as much of the supernatant as possible. Separate the remaining liquid-floc by centrifugation, decant the supernatant and combine the floc together in a 400 mL beaker. Dry overnight in the oven at 110°C or freeze dry if possible. Transfer the dry floc to a 150 mL teflon (FEP) beaker. Add 10 mL of conc. HNO_3 very slowly with constant stirring. When the reaction has stabilized, slowly add 5 mL of HF with stirring followed by 10 mL of HClO_4 . Place the beaker on an asbestos and a ceramic pad on a hot plate and carefully heat to dryness. Add a further 5 mL of HClO_4 and again heat to dryness. Proceed as under "Analytical" for ^{210}Po .

6. Filter Paper (MF-Millipore)

Place the sample in a 150 mL teflon (FEP) beaker, add 30 mL of conc. HNO_3 and place on an asbestos and a ceramic pad on a hot plate. Cover the beaker with a watch glass, heat at low temperature and digest until the filter paper is decomposed. Add 5 mL of HF, 10 mL of HClO_4 , U, Th, Po and stable Pb tracers and heat uncovered to fumes of perchloric. Evaporate to dryness, add another 5 mL of HClO_4 and evaporate to dryness again. Proceed as under "Analytical" for ^{226}Ra or ^{210}Po .

7. AMP (Ammonium Molybdophosphate)

Place the AMP sample (pH 1.5) in a 4 L beaker and allow the AMP to settle. By either decantation or siphoning with a glass U-tube, remove as much of the supernatant as possible. Centrifuge the remaining sample, decant the supernatant and transfer the AMP to a 100 mL beaker. Oven dry at 110°C, and determine the dry weight. Weigh as much as possible into a plastic petri dish, seal and count for ^{134}Cs and ^{137}Cs on a Ge(Li) detector.

8. Mn Fibers

There is no sample preparation required for Mn fiber samples. Place the wet fiber in the radon deemanation bottle and cover with 100 mL of 6 N HCl. Flush the sample with He, seal the bottle and allow ^{222}Rn to grow in for at least 4 days. Proceed as under "radon extraction" in the analysis of ^{226}Ra .

ANALYTICAL

1. Radium-226

(i) Radon Grow-in

Add 100 mL of 0.15 M EDTA to the digested sample, cover the beaker and heat to boiling on a hot plate. Continue heating until all the sample has dissociated and is no longer in the form of a hard cake. Cool and adjust the pH to 10-10.5 using 10 N NaOH. Cover the beaker and reheat to boiling on a hot plate. Transfer the cooled sample to a radon emanation bottle (Canlab 87545-250) rinsing the beaker with a few mL of 0.15 N EDTA solution. Attach inlet and outlet bubbling tubes to the bottle (Fig. 2), connect the outlet hose to the helium line, and bubble helium through the sample for 20 min to remove all radon gas. Several samples may be connected in series and degassed in this manner at the same time. Starting with the last sample in the chain, disconnect the samples from the helium line before turning the gas off and record the time and date on each sample bottle label. Close the sample hose clamps, connect the inlet and outlet sample bubbler tubes, and allow radon to grow-in for at least 4 days.

(ii) Radon Extraction

Turn on the cold finger one-half hour before the extraction is to begin and ensure that the zinc-drierite-ascarite column is sufficiently charged. Place the charcoal column in the dewar containing antifreeze and the cold finger and cool for 5 min. Connect the column to the system (Fig. 2), hook the "in" and "out" hoses together, open all toggle valves, open the circulation valve, close the helium valve and evacuate the system by opening the vacuum valve. Close the vacuum valve and fill the system to 1 atmosphere ("0" on pressure gauge) with helium. Close the bypass toggle valve and the

"in" and "out" toggle valves. Connect the sample to the "in" and "out" hoses and open the sample container to the system. Open the "in" and "out" toggle valves. Turn on the circulation pump and start the gas flow through the system by slowly closing the circulation valve. Record the start time and date and continue the radon extraction for 45-60 min at a flow of 1-2 L/min. For delldrum samples, the extraction is to be carried out at a flow rate of 2-3 L/min for a period of 6 hours. Close the "in" and "out" toggle valves, open the circulation valve, turn off the circulation pump and disconnect the sample from the system. Close the sample hose clamps, connect the "in" and "out" sample bubbler tubes together and record the time and date on the sample bottle. Disconnect the drying column from the charcoal column and evacuate the system for 1-2 min. Disconnect the charcoal column, remove from the cold bath, and allow to come to room temperature.

(iii) Radon Transfer

Connect the charcoal column and the scintillation cell to the radon transfer board (Fig. 3). Ensure that the cell background and efficiency are known. Turn the 4-way valve to evacuate the counting cell, open the round knob shut-off valve and the toggle valve, open the metering valve 2-3 turns and evacuate the system by turning the 3-way valve to the vacuum line. Close the toggle valve and the round knob shut-off valve. Slowly switch the 3-way valve to the helium line until the pressure gauge indicates 15 in/vac, then switch the valve to the off position. Place the charcoal column in the oven at 450°C, turn the 4-way valve such that the counting cell is on line with the charcoal column, open the toggle valve and leave the system untouched for 5 min. Slowly fill the cell to 1 atmosphere (0 on pressure gauge) by opening the round knob shut-off valve, turning the 3-way valve to the helium line and

adjusting the helium flow with the metering valve so that the procedure takes 1-2 min. Remove the cell from the system and evacuate the column by turning the 3-way valve to the off position and the 4-way valve to the vacuum line. Record the cell fill time and date.

(iv) Cell Counting

Allow the counting cell to sit for 4 hours to allow ^{222}Rn and daughters ^{218}Po and ^{214}Po to reach equilibrium. Place the cell in the scintillation counter making sure that it is properly aligned, turn the counter on, and count until the desired statistics are reached. Record the time and date when the count is started. When counting is complete, evacuate the cell and refill with helium.

(v) EDTA Digestion

After the ^{226}Ra analysis is complete, it is necessary to destroy the EDTA complex before the next step in the analysis is carried out.

Transfer the sample to a 250 mL glass beaker. Add 30 mL of conc. HNO_3 and evaporate to dryness. Reduce heat near dryness to control splattering of the sample. Place the sample in a muffle furnace overnight at 400°C and cool. Add 10 mL of conc. HNO_3 , 10 mL of HClO_4 and evaporate to dryness on a hot plate. Continue with the analysis of ^{210}Po .

(vi) Cell Background Determination

Evacuate an unused counting cell and refill with helium. Count on the scintillation counter to determine background counts per minute.

(vii) Cell Efficiency

Use an NBS ^{226}Ra standard of known activity as a sample and carry out the analysis for ^{226}Ra as described above.

$$\text{Cell efficiency} = \frac{^{226}\text{Ra activity found}}{^{226}\text{Ra activity known}}$$

2. Polonium-210

Add 75 mL of 10 N HCl to the sample in a 125 mL erlenmeyer flask, cover with a watch glass and place on a hot plate at low heat to dissolve most of the solids. If the presence of iron is suspected or indicated by a yellow color in the acid phase proceed as under "Fe Removal." If no iron is present, proceed as under "Autodeposition of Polonium."

(i) Fe Removal

Decant the liquid sample into a 250 mL separatory funnel. Extract iron with 50 mL aliquots of iso-propyl ether until no yellow color appears in the organic phase. Place the used iso-propyl ether in the waste bottle for redistillation. Return the liquid sample to the original container and evaporate to dryness on a hot plate. Add 50 mL of 10 N HCl, cover with a watch glass, and heat gently for 2 min. If a yellow color persists in the liquid phase, repeat the ether extraction until no yellow color is transferred to the organic phase, evaporate to dryness, and redissolve in 10 N HCl. If the sample contains any undissolved material, filter (0.45 μ m) and save the filtered material. Proceed with the "Autodeposition of Polonium."

(ii) Autodeposition of Polonium

Using the "Vibro Graver," clearly etch the sample identification number and isotope to be plated on one side of an unused silver disc and place it in the sample container with the unmarked side up. Cover the sample flask with a watch glass and place on a hot plate. Heat the sample overnight at 70-80°C. After cooling the sample to room temperature, carefully remove the silver disc using a plastic spatula, and rinse with (d)H₂O. Count the disc on the alpha spectrometer. Continue processing the sample as under "U/Th/Pb Separation."

3. Uranium-238, 234; Thorium-232, 230; Lead-210

(i) U/Th/Pb Separation

Prepare an ion exchange column 15 cm x 2.5 cm containing Bio Rad AG1-X2, 100-200 mesh anion exchange resin in 10 N HCl. Pass the sample through the column followed by 100 mL of 10 N HCl. Collect and label the eluant as the Th/Pb fraction; U is retained on the column. Elute and collect the U fraction by passing 150 mL of 1.5 N HCl through the column.

Evaporate the Th/Pb fraction to dryness on a hot plate taking care to control the temperature near the end to prevent the sample from baking. Add 50 mL of 1.5 N HCl, cover with a watch glass, and heat on a hot plate to redissolve the sample. If any undissolved material remains, filter (0.45 μ m) and save the filtered material.

Pass the Th/Pb fraction through the same column and follow with 100 mL of 1.5 N HCl. Collect and label the eluant as the Th fraction. Lead is retained on the column. Elute and collect the Pb fraction by passing 150 mL of 10 N HCl through the column. The column is now in 10 N HCl and ready for the next sample.

(ii) Uranium Fraction

Evaporate the U fraction on a hot plate to \approx 30 mL, transfer to a 50 mL beaker, and evaporate to dryness. Add 5 mL of 2 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and heat on a hot-plate for 1 minute at low heat. Transfer the sample to a 16 x 100 mm test tube and extract uranium into three 3 mL aliquots of ethyl acetate. For each extraction, add the ethyl acetate, stopper the test tube with a neoprene stopper, shake vigorously for several minutes and allow the organic and inorganic phases to separate. The organic phase can be collected using a 2 mL disposable pipette. Combine the ethyl acetate portions in an 18 x 150 mm test

tube and back extract the uranium into two 5 mL aliquots of (d)H₂O using the same procedure as for the previous ethyl acetate extractions. Combine the (d)H₂O portions in the 50 mL beaker and evaporate to dryness. Add 5 mL of (d)H₂O, heat to redissolve solids, and adjust the pH to 3.5-4.0 using 6 N HCl or 5 N NaOH. Transfer the sample to a 13 x 100 mm test tube, add 0.5 mL of 0.25 M TTA, stopper and shake vigorously for several minutes to extract uranium into the TTA. Centrifuge for 5 min at 3000 rpm to separate the organic-inorganic phases. Clearly label one side of a stainless steel plating disc with a "Vibro-Graver." Indent the center of the disc using a hammer and counter punch and place on a hot plate at medium heat. Remove the TTA from the sample using a disposable glass pipette and add dropwise to the center part of the disc. Increase the temperature of the hot plate until all liquid on the disc disappears. Remove the disc from the hot plate with preheated tweezers and slowly, to avoid combustion, heat to red hot over a blast burner. Cool the disc on an asbestos pad, remove the indentation with a hammer, and count on the alpha spectrometer.

(iii) Thorium Fraction

Evaporate the thorium fraction on a hot plate to ≈30 mL, transfer to a 50 mL beaker and heat to dryness. Add 30 mL of 2.2 M Al(NO₃)₃•9H₂O, cover with a watch glass, and heat on medium heat to dissolve the sample. Transfer to a 250 mL separatory funnel, add 25 mL of Aliquat 336, stopper and shake vigorously for several minutes. Draw off the aqueous portion into the original beaker and collect the organic part in a clean beaker. Return the aqueous portion to the separatory funnel and repeat the extraction with Aliquat 336 two more times. Discard the aqueous portion and recombine the organic portions in the separatory funnel. Add 25 mL of 8 N HNO₃, stopper and

shake well for several minutes. Discard the aqueous portion and repeat once more. Add 25 mL of 10 N HCl to the separatory funnel, stopper, and shake vigorously for several minutes. Collect the aqueous portion in a 250 mL beaker and repeat the extraction twice more. Discard the organic layer and combine the aqueous portions in the beaker. Add 10 mL of conc. HNO_3 and 5 mL of HClO_4 . Evaporate the sample on a hot plate to ≈ 30 mL, transfer to a 50 mL beaker and heat to dryness. Add 5 mL of (d) H_2O and heat to dissolve any solids. Adjust the pH to ≈ 2 using 6 N HCl and 5 N NaOH and transfer the sample to a 13 x 100 mm test tube. Add 0.5 mL of 0.25 M TTA and prepare the counting disc as described for the U fraction.

(iv) Lead Fraction

Evaporate the lead fraction to ≈ 30 mL on a hot plate. Transfer the sample to a 50 mL graduated cylinder and make up to 50 mL with 1.5 N HCl. Store in a 60 mL plastic bottle, record the date of lead separation and allow ^{210}Po to grow-in for at least one half-life (138 days). Transfer the sample to a 125 mL erlenmeyer flask and add the polonium tracer using an eppendorf pipette. Take a 1000 μL aliquot of the sample, dilute to 100 mL with (d) H_2O and analyze for stable lead by atomic adsorption spectroscopy. Prepare the polonium counting disc as described previously under "Autodeposition of Polonium" and count on the alpha spectrometer.

CALCULATIONS

1. Radioactive Growth and Decay (Friedlander et al. 1981)

The activity of any radioisotope can be expressed by the exponential law:

$$A = A_0 e^{-\lambda t} \quad (1)$$

where A = new activity after decay of time t

A_0 = initial activity

λ = decay constant

The half-life ($T_{1/2}$) of an isotope is the amount of time required for a given activity to decrease by one-half. Substituting $T_{1/2} = t$ in equation

1 we have:

$$\frac{A}{A_0} = e^{-\lambda T_{1/2}}$$

$$\lambda = \frac{0.6932}{T_{1/2}} \quad (2)$$

2. Radium-226

The activity of ^{226}Ra is calculated from equation 3 (Rushing et al. 1963) which accounts for the in-growth of ^{222}Rn , the decay of ^{222}Rn after it is removed from its parent, the decay of ^{222}Rn over the counting period, the contribution from ^{222}Rn decay products, cell background and counting efficiency. Radon and daughters must be in equilibrium.

$$A_{\text{Ra}} = \frac{\text{Ca}-\text{Cb}}{\text{Eff.} \times 3} \times \frac{1}{(1-e^{-\lambda_1 t_1})} \times \frac{1}{e^{-\lambda_1 t_2}} \times \frac{\lambda_1 t_3}{(1-e^{-\lambda_1 t_3})} \quad (3)$$

where:

A_{Ra} = Radium-226 activity in disintegrations per second (dps)

Ca = observed counts per second

Cb = cell background counts per second

Eff. = cell efficiency

λ_1 = decay constant for ^{222}Ra (days)

t_1 = time interval for radon growth (days)

t_2 = time interval between deenamation and counting (days)

t_3 = time interval of counting (days)

Another approach to determining ^{226}Ra is to solve the Bateman equations (Friedlander et al. 1981; Sarmiento et al. 1976) for each of ^{222}Rn , ^{218}Po , and ^{214}Po . This would enable the cell to be counted immediately after filling and would correct for the disequilibrium between ^{222}Rn and its daughters (^{218}Po and ^{214}Po). In this case:

$$A_1 = A \int_{t_2}^{t_4} (e^{-\lambda_1 t}) dt$$

$$= AK_1$$

$$A_2 = A \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} \right) \int_{t_2}^{t_4} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) dt$$

$$\begin{aligned}
 &= AK_2 \\
 A_4 &= A(\lambda_2\lambda_3\lambda_4) \int_{t_2}^{t_4} \left(\frac{e^{-\lambda_1 t}}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)(\lambda_4-\lambda_1)} + \frac{e^{-\lambda_2 t}}{(\lambda_1-\lambda_2)(\lambda_3-\lambda_2)(\lambda_4-\lambda_2)} \right. \\
 &\quad \left. + \frac{e^{-\lambda_3 t}}{(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)(\lambda_4-\lambda_3)} + \frac{e^{-\lambda_4 t}}{(\lambda_1-\lambda_4)(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)} \right) dt \\
 &= AK_4
 \end{aligned}$$

where:

$$t_4 = t_2 + t_3$$

A_1, A_2, A_4 are the activities of $^{222}\text{Rn}, ^{218}\text{Po}$ and ^{214}Bi respectively;

$A_4 = A_5 =$ activity of ^{214}Po (due to short $T_{1/2}$);

$\lambda_1, \lambda_2, \lambda_3, \lambda_4$ are the decay constants for $^{222}\text{Rn}, ^{218}\text{Po}, ^{214}\text{Pb}$ and ^{214}Bi respectively;

A is the activity of ^{222}Rn at time cell was filled.

$$A_1 + A_2 + A_4 = \text{Total activity}$$

$$= \frac{(Ca-Cb)}{\text{Eff.}}$$

By correcting for radon growth, A becomes the ^{226}Ra activity.

$$A_{\text{Ra}} = \frac{Ca-Cb}{\text{Eff.}} \times \frac{1}{(1-e^{-\lambda_1 t_1})} \times \frac{1}{(K_1+K_2+K_4)} \quad (4)$$

3. Uranium Isotopes

$$A_U = \frac{\Sigma U \times U \cdot TR}{\Sigma U \cdot TR} \quad (5)$$

where:

A_U = activity (dps) of the uranium isotope

$U \cdot TR$ = total activity of the uranium isotope tracer (dps)

ΣU = total counts in uranium isotope peak

$\Sigma U \cdot TR$ = total counts in the uranium isotope tracer peak

4. Thorium Isotopes

$$A_{Th} = \frac{[\Sigma Th - (0.064 \times \Sigma Ra)] \times Th \cdot TR}{\Sigma Th \cdot TR} \quad (6)$$

where:

A_{Th} = activity (dps) of the thorium isotope

$Th \cdot TR$ = *total activity of the thorium isotope tracer (dps)

ΣTh = total counts in the thorium isotope peak

ΣRa = **total counts in the ^{224}Ra peak

$\Sigma Th \cdot TR$ = total counts in the thorium isotope tracer peak

* When ^{228}Th is used as the isotopic tracer, the value for $Th \cdot TR$ must be the sum of the activities (dps) of the added tracer and the naturally occurring ^{228}Th in the sample as determined by gamma counting.

** 6% of the ^{224}Ra alpha emissions occur at 5.45 MeV which are included in the ^{228}Th peak and must be subtracted from ΣTh .

5. Polonium-210

$$A_{Po} = \frac{\Sigma Po \times Po \cdot TR}{\Sigma Po \cdot TR} \times \frac{1}{e^{-\lambda t_1}} \quad (7)$$

where:

A_{Po} = Po-210 activity (dps) at time of plating

$Po \cdot TR$ = Po tracer activity (dps) on counting day

ΣPo = total counts in ^{210}Po peak

$\Sigma Po \cdot TR$ = total counts in tracer peak

λ = decay constant for ^{210}Po (days)

t_1 = number of days between plating and counting.

6. Lead-210

Lead-210 is determined by separating Po and Pb and growing in ^{210}Po over a known period of time. The ^{210}Po activity is calculated from equation 7 and ^{210}Pb is calculated from equation 8.

$$A_{\text{Pb}} = \frac{A_{\text{Po}}}{Y_{\text{Pb}}} \times \frac{1}{(1 - e^{-\lambda t_2})} \quad (8)$$

where:

A_{Pb} = activity of ^{210}Pb (dps)

A_{Po} = activity (dps) of ^{210}Po at time of plating

Y_{Pb} = Pb recovery as determined by atomic absorption

$$= \frac{\text{Pb recovered (mg)}}{\text{Pb added (mg)}}$$

λ = decay constant for ^{210}Po (days)

t_2 = time (days) elapsed between Pb separation and Po plating

7. Cesium-137 and Thorium-228

The activities of ^{137}Cs and ^{228}Th are determined from the gamma spectrum obtained by counting the sample with a Ge(Li) detector. The ^{137}Cs activity is obtained from the 662 KeV peak (85.0%) of $^{137\text{m}}\text{Ba}$ and is decay corrected back to the sampling day.

$$(1) \quad A_{\text{Cs}} = \frac{\Sigma\text{Cs}}{0.85 \times \text{Eff}_{137}} \times \frac{1}{e^{-\lambda t}} \quad (9)$$

where:

A_{Cs} = activity of ^{137}Cs at time of sampling (dps)

ΣCs = counts per second (cps) of 662 KeV photo peak.

Eff_{137} = counting efficiency for ^{137}Cs at 662 KeV for the sample geometry used

λ = decay constant for ^{137}Cs (years)

t = elapsed time (yr) between sampling and counting

For AMP floc:

$$A_{\text{Cs}} = \frac{\Sigma\text{Cs}}{0.85 \times \text{Eff}_{137}} \times \frac{1}{e^{-\lambda t}} \times \frac{1}{R} \quad (10)$$

where:

R = Cs recovery determined from the ^{134}Cs tracer

$$= \frac{\text{cps at 605 KeV } (^{134}\text{Cs}) \text{ observed}}{\text{cps at 605 KeV } (^{134}\text{Cs}) \text{ theoretical}}$$

(2) The activity of ^{228}Th is determined from its daughter, ^{212}Pb , which has a gamma peak at 239 KeV (43%).

$$A_{\text{Th}} = \frac{\Sigma\text{Th} - \text{Bkg}}{0.43 \times \text{Eff}_{228}}$$

where:

A_{Th} = activity of ^{228}Th (dps)

Σ_{Th} = cps in the 239 KeV photo-peak

Eff_{228} = counting efficiency for ^{228}Th at 239 KeV for sample geometry used

Bkg = detector background (cps) at 239 KeV.

8. Polonium-210 Correction

The state of equilibrium between ^{210}Po and ^{210}Pb cannot be predicted for many samples. As samples are not analyzed immediately, the ^{210}Po values must be corrected when not in equilibrium with ^{210}Pb .

(i) If the measured ^{210}Po activity (A_{Po}) is less than the measured ^{210}Pb activity (A_{Pb}), then the value for ^{210}Po includes ^{210}Po activity grown in from ^{210}Pb over time, t . The ^{210}Po has also decayed over time (t).

t = time interval (days) from the sampling day to the day polonium is plated on the silver disc.

$$\text{corrected } A_{\text{Po}} = [A_{\text{Po}} - (A_{\text{Pb}} \times (1 - e^{-\lambda t}))] / e^{-\lambda t} \quad (12)$$

where λ = decay constant for ^{210}Po (days).

(ii) If A_{Po} is greater than A_{Pb} , then ^{210}Po was in excess of ^{210}Pb and has decayed over time, t .

$$\text{corrected } A_{\text{Po}} = [(A_{\text{Po}} - A_{\text{Pb}}) / e^{-\lambda t}] + A_{\text{Pb}} \quad (13)$$

Note: Iron floc samples contain only a fraction of the total ^{210}Pb activity as determined by the Pb yield determination which is carried out on the separated Pb fraction. The A_{Pb} value used in equations 12 and 13 must be multiplied by the fraction of Pb recovered as determined at the time polonium is plated on the silver disc. This will give the amount of ^{210}Pb in the floc sample.

(iii) Unaccountable uncertainties

Polonium-210 is determined using a Po tracer which accounts for Po recovery in the analysis. The recovery at each step is not determined. In Fe

floc samples, the Po tracer also corrects for the Po recovery in the floccing procedure at the time the sample was taken. When $A_{Po} < A_{Pb}$, the amount of ^{210}Po that grows in from the ^{210}Pb between the time of sampling and plating is also subjected to this correction. This results in an inflated value for ^{210}Po .

9. Errors

For nuclear counting, the standard deviation (σ) of n counts is calculated as the square root of the number of counts (\sqrt{n}) and the count value would be expressed as $n \pm \sqrt{n}$ (1σ). Similarly a count rate of n/t , where t is the elapsed count time in seconds, is expressed as $n/t \pm \sqrt{n}/t$.

Errors are propagated in mathematical formulas according to the following conventions:

Consider two sets of counts a and b having errors of

$$\sigma_a = \sqrt{a} \text{ and } \sigma_b = \sqrt{b}$$

(i) For a formula $a + b$, the error (1σ) is:

$$\sigma_{a+b} = (\sigma_a^2 + \sigma_b^2)^{1/2} \quad (14)$$

(ii) For a formula $a \times b$, the error (1σ) is:

$$\sigma_{ab} = (\sigma_a^2 b^2 + \sigma_b^2 a^2)^{1/2} \quad (15)$$

(iii) For a formula a/b , the error (1σ) is:

$$\sigma_{a/b} = \frac{a}{b} \left[\left(\frac{\sigma_a}{a} \right)^2 + \left(\frac{\sigma_b}{b} \right)^2 \right]^{1/2}$$

Using these three equations, it is possible to calculate the errors for each isotope.

Example:

2.67 ± 0.17 (1σ) Bq of ^{209}Po was added as a tracer to a 3.0015 g. sediment sample which was analyzed for ^{210}Po . The alpha spectrum showed 9540 counts in the ^{209}Po peak and 3095 counts in the ^{210}Po peak. The time interval from plating on the silver disc to counting was 15 days.

From equation 7:

$$A_{\text{Po}} = \frac{3095 \times 2.67}{9540} \times \frac{1}{e^{-15\lambda}}$$

$$\text{where } \lambda = \frac{0.6931}{138.4}$$

$$A_{\text{Po}} = 9.34 \times 10^{-1} \text{ Bq. or } 3.11 \times 10^{-1} \text{ Bq/g.}$$

The error in A_{P_0} can be determined in two steps.

(i) Using equation 15:

$$A_{P_0} = \frac{8263.65 \pm [(\sqrt{3095} \times 2.67)^2 + (3095 \times 0.17)^2]^{1/2}}{9540 \pm 97.67} \times \frac{1}{e^{-15\lambda}}$$
$$= \frac{8263.65 \pm 546.72}{9540 \pm 97.67} \times \frac{1}{e^{-15\lambda}}$$

(ii) Using equation 16:

$$\sigma_{A_{P_0}} = \pm \frac{8263.65}{9540} \left[\left(\frac{546.72}{8263.65} \right)^2 + \left(\frac{97.67}{9540} \right)^2 \right]^{1/2} \times \frac{1}{e^{-15\lambda}}$$
$$= \pm 6.25 \times 10^{-2} (1\sigma)$$

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