

CHAPTER III

EXPERIMENTAL

3.1 Materials.

3.1.1 Reagents. Unless otherwise stated, all chemicals are of analytical reagent grade.

An alkaline EDTA solution was prepared by dissolving 10 g of the disodium salt of ethylenediaminetetra acetic acid and 10 g of sodium carbonate in 1 dm³ demineralised water. This solution was used for cleaning all glasswares for de-emanation.

Chromatographic grade silica gel, particle size of 35-70 mesh was dried in an oven at 120°C for 10 hours before use.

Liquid scintillator was prepared by dissolving 4 g of 2,5 Dimethyloxazole (PPO) and 0.1 g of 1,4-bis-2-(4-Methyl-5-Phenyloxazolyl)-Benzene (Dimethyl POPOP) in 1 dm³ toluene.

A standard solution containing 1.9273×10^{-4} Pci g⁻¹ of Ra-226 was purchased from the National Bureau of standard (NBS), Washington, D.C., U.S.A. A stock solution of 52.6 Pci cm⁻³ was prepared by weighing 1.3642 g of the radium standard solution into 10 cm³ of concentrated nitric acid and the solution was made to 500 cm³ by the addition of water. This stock solution was stored for use for 5 months. It is used for the determination of counting conditions, de-emanation conditions and the limit of detection.

An alcoholic liquid nitrogen slurry as a cooling solution for the radon-trap was prepared by adding 125 cm³ of ethanol into a

500 cm³ dewar flask. Liquid nitrogen in 50 cm³ portion, was added with stirring into ethanol until a thick slurry was obtained.

3.1.2 Samples.

3.1.2.1 Standard uranium ore samples.

A standard uranium ore from the New Brunswick Laboratory (NBL), New Jersey, U.S.A. NBL 74 A, was analysed to confirm the accuracy of the method. The ore contains 0.1 per cent uranium, with a ratio of 3.44×10^{-7} gram of radium-226 to gram of uranium at equilibrium.

3.1.2.2 Monazite samples.

Fifteen monazite samples from different tin mines in the southern part of Thailand were analysed. These samples were purified to 90 per cent by the Department of Mineral Resources, Thailand. The codes and the sampling sources were tabulated in Table 3.1

Table 3.1 The codes and sampling sources of the monazite samples.

Code	Sampling Source	Province
PG2	Zoo Khun Luang Mine	Pang nga
PG3	Khao Kata Tong Mine	Pang nga
PG4	Sup Rung Ruang Mine	Pang nga
RN1	Sang Tong Mine	Ranong
RN2	Sang Tong Mine	Ranong
RN 3	Anuparp and Son Mine	Ranong
RN4	S.A. Mineral Mine	Ranong
RN6	Khun Manoon Mine	Ranong
RN8	Rattanaset Ranong Kha Rae Mine	Ranong
TK1	Toong Kamin Tong Mine	Amphur Takua Pa, Pang nga
TK2	Toong Kamin Tong Mine	Amphur Takua Pa, Pang nga
TK3	J.T. Mineral Mine	Amphur Takua Pa, Pang nga
TK5	Hok Jong Seng Mine	Amphur Takua Pa, Pang nga
Tk7	Boon Soong Mine	Amphur Takua Pa, Pang nga
Tk8	Boon Soong Mine	Amphur Takua Pa, Pang nga

3.2 Apparatus and Instrument.

3.2.1 Apparatus for digestion of monazite samples.

A 100 cm³ conical flask with a rubber stopcock and an air condenser made of a pyrex tube (10 mm in diameter and 50 cm in length) was used as a reaction vessel. The vessel was placed on a magnetic

stirrer-hot plate and the content was stirred during digestion. The temperature of the reaction mass was measured by a thermometer. The schematic diagram of the digestion apparatus is shown in Figure 3.1

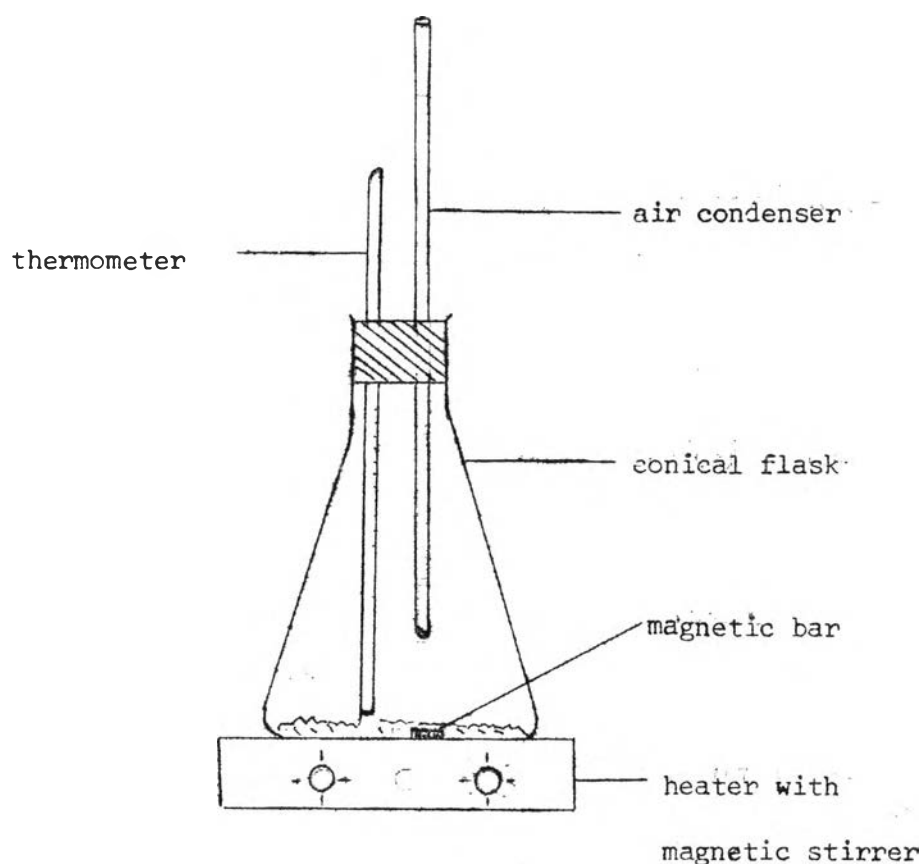
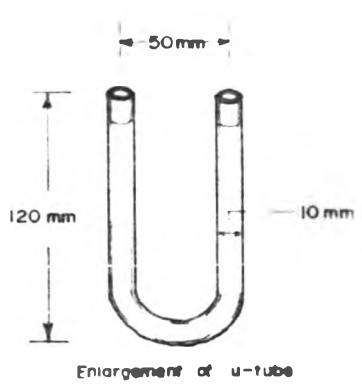
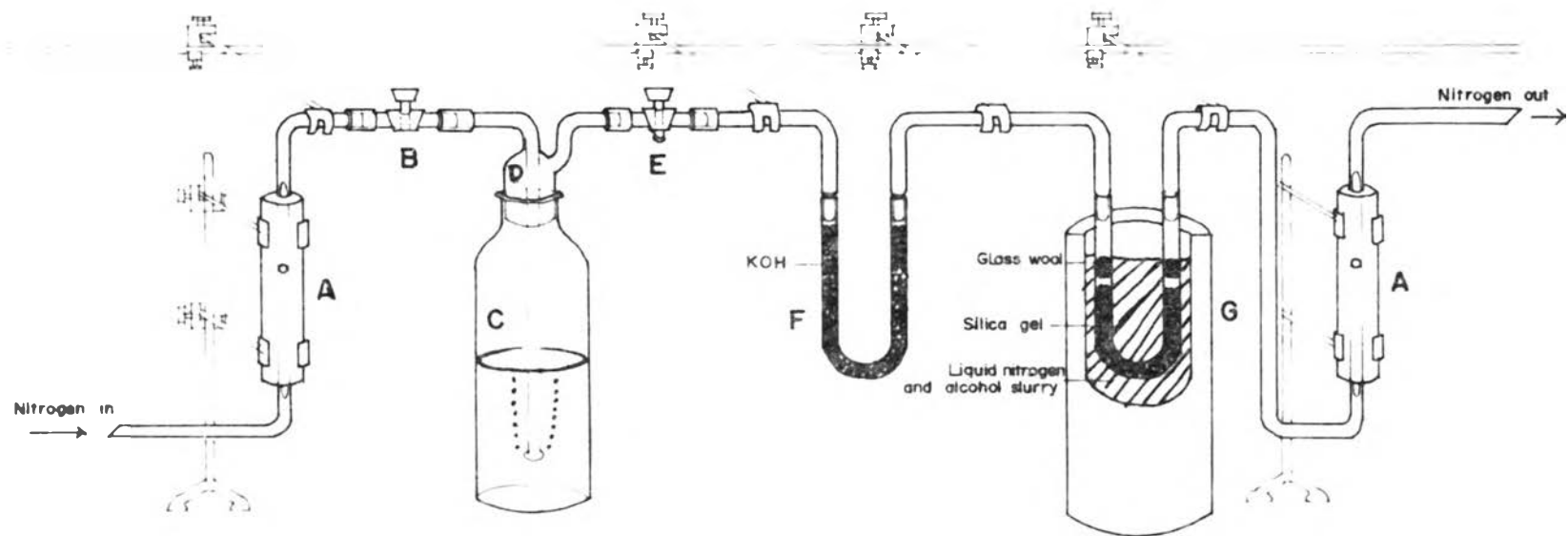


Figure 3.1 Schematic diagram of the digestion apparatus.

3.2.2 Apparatus for de-emanation and trapping of radon.

The experimental set up of the de-emanation and trapping line is shown in Figure 3.2

The de-emanation flask is a 500 cm³ gas washing bottle with a $\frac{24}{29}$ ground-glass neck. The inlet tube, 6 mm diameter, reaches nearly



- A : Flow meter
- B : Inlet stopcock
- C : De-emanation flask
- D : De-emanation head
- E : Outlet stopcock
- F : Water trap u-tube
- G : Radon trap u-tube

Figure 3.2 Apparatus for de emanation and trapping of radon.

to the bottom of the de-emanation flask. The bottom end of the inlet tube has a funnel shape with holes of 1 mm in diameter on it to break up the current of gas into a stream of fine bubbles. The outlet tube is a 6 millimeters diameter glasstube. A plug bore 3 millimeters vacuum stopcock is sealed to the upper ends, outside of the flask, of both the inlet and the outlet tubes. The flask is connected to the system by vacuum-pressure type rubber tubing. Thus, the flask as a unit can be de-emanated and removed from the system to await for radon build up.

The water vapor trap is a 10 mm diameter by 120 mm U-tube with $\frac{14}{23}$ ground-glass joints. It is connected to the system by vacuum pressure type rubber tubing through 10 mm diameter glass tube.

The radon-trap is similar to the water vapor trap except that at the time of operation it is cooled by dipping into a 500 cm³ dewar flask containing liquid nitrogen.

A flowmeter with a maximum flow capacity of 500 cm³ min⁻¹ is connected to each terminal of the line to control constant flow rate of the carrier gas. A difference in the flow rate between the two flow meters means that a leak has developed in the line.

3.2.3 Radiation counting instrument.

A liquid scintillation spectrometer from Packard, Tri-carb model 2425, was used for radiation measurement. The block diagram and a picture of the liquid scintillation spectrometer are shown in Figure 3.3 and Figure 3.4, respectively.

3.3 Sample Preparation

3.3.1 Standard uranium cre.

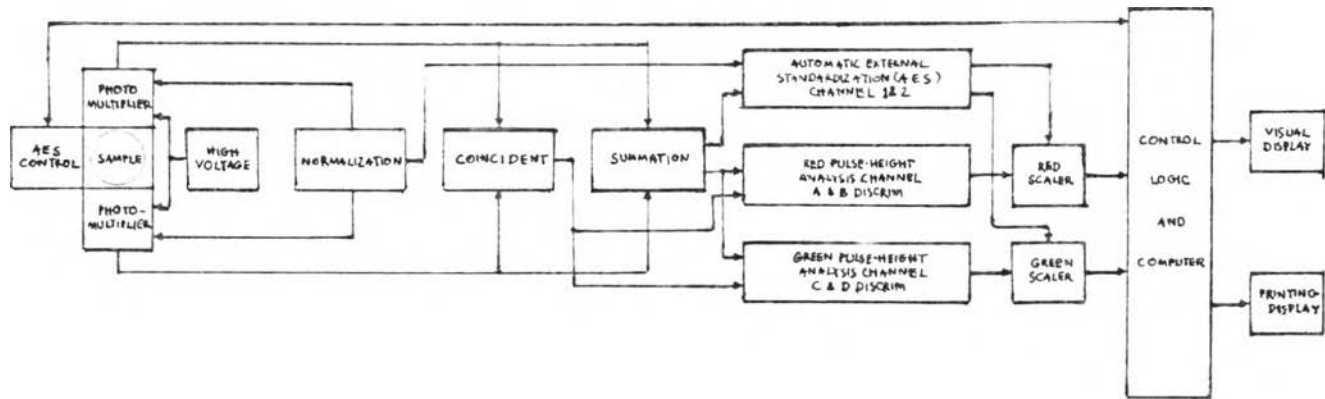


Figure 3.3 Block diagram of liquid scintillation spectrometer

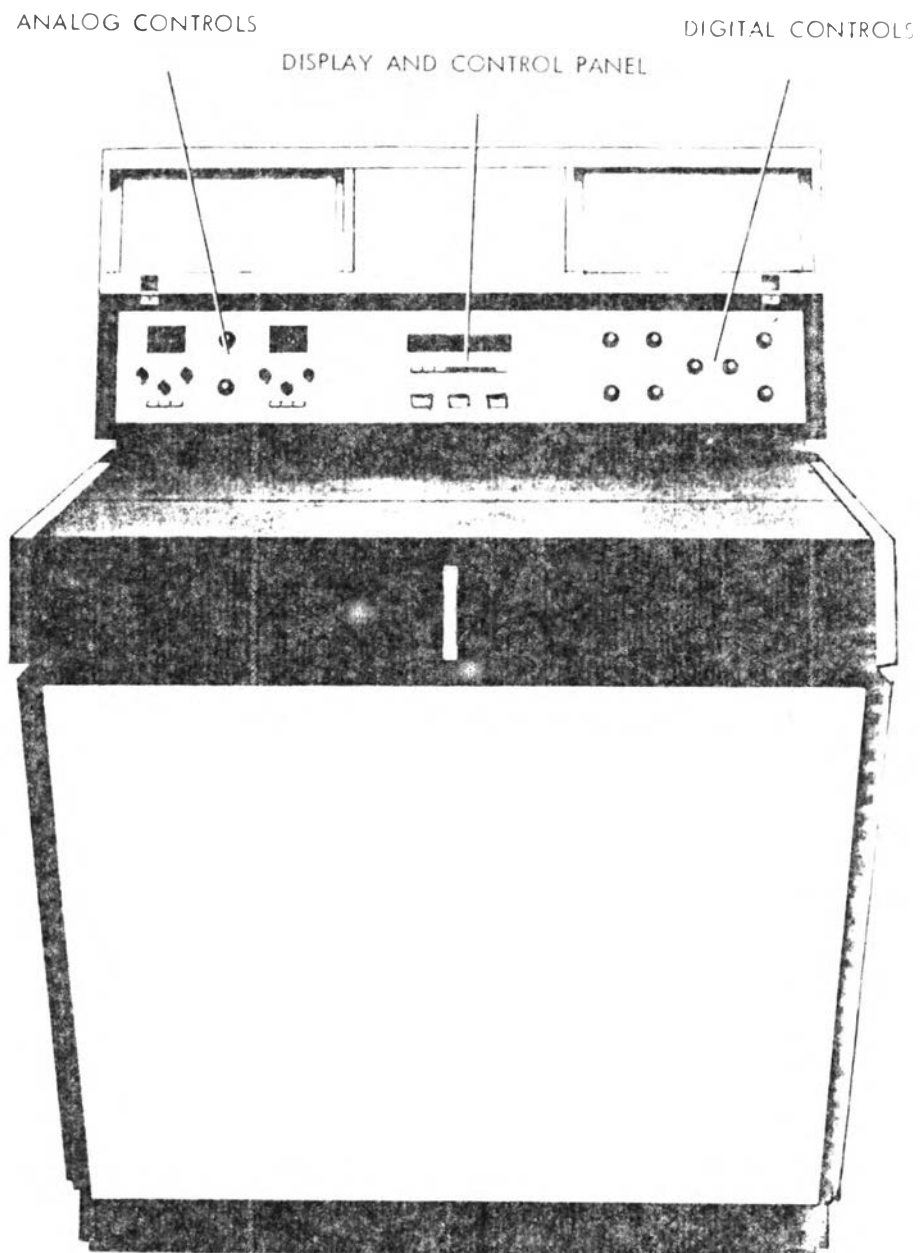


Figure 3.4 Model 2425 Tri-carb liquid scintillation spectrometer.

Five samples of the standard uranium ore (NBL74A) were weighed at the range of 0.1 to 0.5 g into 50 cm³ teflon beakers. The radium content of the samples varied between 42.5 to 190.0 Pci. The samples were digested by 40 cm³ of a mixture of acid containing 40% hydrofluoric acid, concentrated perchloric acid and concentrated nitric acid in a ratio of 10:5:1 (28). After the completion of digestion the solution was poured into a de-emanation flask, and the acidity was adjusted to 0.3 mol/l in nitric acid. The total volume of the solution was made to 300 cm³. The head of the de-emanation flask with the two stopcocks in close position was put to the neck of the de-emanation flask.

3.3.2 Monazite Samples.

The monazite samples were ground to minus 100 mesh by an automatic grinder. For each digestion a weight of 2 to 3 g was used. The sulphuric acid digestion(29) was applied. Complete digestion was obtained by allowing the samples to react with 96.5 percent sulphuric acid at 210^oc for 2 hours, with an acid to sand sample ratio of 3 to 1. After digestion a thick and gray paste of reaction mass was obtained which was cooled to 70^oc. Cool demineralised water was added in a ratio of 9 parts of water to 1 part of sand (weight by weight). The resulting monazite sulphate solution was filtered through a whatman number 42 filter paper to remove the gangue. The clear solution was poured into a de-emanation flask. A portion of 6 cm³ of concentrated nitric acid was added into the solution and the total volume was made to 300 cm³ by de-mineralised water. The head of the de-emanation flask with its **two stopcocks** in close position was then put to the neck of the de-emanation flask.

3.4 Procedure.

3.4.1 First de-emanation.

First de-emanation must be performed to remove unsupported radon before the start of ingrowth period. The ingrowth of radon from radium-226 as a function of time is given in Table 3.2 (3).

The de-emanation and trapping line were set up as shown in Figure 3.2. The water vapor trap and the radon trap were, however, empty. After the stopcocks were turned to the open position, nitrogen gas with a flow-rate of $200 \text{ cm}^3 \text{ min}^{-1}$ was allowed to pass through the line for 1 hour. Then the nitrogen flow was stopped and the stopcocks were turned to close position. The de-emanation flask was disconnected from the line and placed aside for ingrowth of radon.

3.4.2 Second de-emanation.

The water-vapor trap filled with 12 g of KOH pellets was connected to the line. The radon-trap filled with silica gel with inert glass-wool plugs on top of the layers was connected to the line and dipped into a dewar containing the alcoholic liquid nitrogen slurry. The de-emanation flask was then connected. After the two stopcocks of the de-emanation flask were turned to the open position, nitrogen gas was allowed to pass through the line for a period of time which was called the de-emanation time. When de-emanation was completed, the nitrogen flow was stopped and the stopcocks were turned to close-position. The dewar flask containing the alcoholic liquid nitrogen slurry was

Table 3.2 Factor for decay of radon-222, growth of radon-222 from radium-226 and correction of radon-222 activity for decay during counting.

Time	Factor for Decay of Radon 222		Factor for Growth of Radon 222 from Radium 226		Factor for Correction of Radon 222 Activity for Decay during Counting
	$A = e^{-\lambda t}$		$B = 1 - e^{-\lambda t}$		$C = \lambda t / (1 - e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours
0.0	1.0000		0.000 00		1.000
0.2	0.9985		0.001 51		1.001
0.4	0.9970		0.003 01		1.001
0.6	0.9955		0.004 52		1.002
0.8	0.9940		0.006 02		1.003
1	0.9925	0.8343	0.007 52	0.1657	1.004
2	0.9850	0.6960	0.014 99	0.3040	1.008
3	0.9776	0.5807	0.022 40	0.4193	1.011
4	0.9703	0.4844	0.029 75	0.5156	1.015
5	0.9630	0.4041	0.037 05	0.5959	1.019
6	0.9557	0.3372	0.044 29	0.6628	1.023
7	0.9485	0.2813	0.051 48	0.7187	1.027
8	0.9414	0.2347	0.058 61	0.7653	1.031
9	0.9343	0.1958	0.065 69	0.8042	1.034
10	0.9273	0.1633	0.072 72	0.8367	1.038
11	0.9203	0.1363	0.079 69	0.8637	1.042
12	0.9134	0.1137	0.086 62	0.8863	1.046
13	0.9065	0.0948	0.093 49	0.9052	1.050
14	0.8997	0.0791	0.100 31	0.9209	1.054
15	0.8929	0.0660	0.107 07	0.9340	1.058
16	0.8862	0.0551	0.113 8	0.9449	1.062
17	0.8795	0.0459	0.120 5	0.9541	1.066
18	0.8729	0.0383	0.127 1	0.9617	1.069
19	0.8664	0.0320	0.133 6	0.9680	1.073
20	0.8598	0.0267	0.140 2	0.9733	1.077
21	0.8534	0.0223	0.146 6	0.9777	1.081
22	0.8470	0.0186	0.153 0	0.9814	1.085
23	0.8406	0.0155	0.159 4	0.9845	1.089
24	0.8343	0.0129	0.165 7	0.9871	1.093
25	0.8280	0.0108	0.172 0	0.9892	1.097

Table 3.2 (continue) Factor for decay of radon-222, growth of radon-222 from radium-226 and correction of radon-222 activity for decay during counting.

Time	Factor for Decay of Radon 222		Factor for Growth of Radon 222 from Radium 226		Factor for Correction of Radon 222 Activity for Decay during Counting
	$A = e^{-\lambda t}$		$B = 1 - e^{-\lambda t}$		$C = \lambda t / (1 - e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours
26	0.8218	0.0090	0.1782	0.9910	1.101
27	0.8156	0.0075	0.1844	0.9925	1.105
28	0.8095	0.0063	0.1905	0.9937	1.109
29	0.8034	0.0052	0.1966	0.9948	1.113
30	0.7973	0.0044	0.2027	0.9956	1.118
31	0.7913	0.0036	0.2087	0.9964	1.122
32	0.7854	0.0030	0.2146	0.9970	1.126
33	0.7795	0.0025	0.2205	0.9975	1.130
34	0.7736	0.0021	0.2264	0.9979	1.134
35	0.7678	0.0018	0.2322	0.9982	1.138
36	0.7620	0.0015	0.2380	0.9985	1.142
37	0.7563	0.0012	0.2437	0.9988	1.146
38	0.7506	0.0010	0.2494	0.9990	1.150
39	0.7449	0.0009	0.2551	0.9991	1.154
40	0.7393	0.0007	0.2607	0.9993	1.159
41	0.7338	0.0006	0.2662	0.9994	1.163
42	0.7283	0.0005	0.2717	0.9995	1.167
43	0.7228	0.0004	0.2772	0.9996	1.171
44	0.7173	0.0003	0.2827	0.9997	1.175
45	0.7120	0.0003	0.2880	0.9997	1.179
46	0.7066	0.0002	0.2934	0.9998	1.184
47	0.7013	0.0002	0.2987	0.9998	1.188
48	0.6960	0.0002	0.3040	0.9998	1.192
49	0.6908	0.0001	0.3092	0.9999	1.196
50	0.6856	0.0001	0.3144	0.9999	1.201
51	0.6804	0.0001	0.3196	0.9999	1.205
52	0.6753	0.0001	0.3247	0.9999	1.209
53	0.6702	0.0001	0.3298	0.9999	1.213
54	0.6652	0.0001	0.3348	0.9999	1.218
55	0.6602	0.0000	0.3398	1.0000	1.222
56	0.6552	0.0000	0.3448	1.0000	1.226
57	0.6503	0.0000	0.3497	1.0000	1.231
58	0.6454	0.0000	0.3546	1.0000	1.235
59	0.6405	0.0000	0.3595	1.0000	1.239
60	0.6357	0.0000	0.3643	1.0000	1.244

replaced by an ice-water bath with a temperature of approximately 0°C called the warm up temperature. The radon trap was allowed to warm up for a period of time, called the warm up time. The trap was then wiped dried and disconnected from the line. The silica gel was poured into a 22 cm^3 glass counting vial containing a certain volume of liquid scintillator. The cap was replaced immediately and the mixture was mixed by shaking.

3.4.3 Counting.

After de-emanation was completed and silica gel was poured into the liquid scintillator, the vials were left aside for a minimum of 3 hours so that the equilibrium between radon and its daughters would be established. During this period, the vials were kept at a certain temperature, for the release of radon from silica gel. The temperature is called the desorption temperature.

The samples were then counted for 100 minutes each. The count rate obtained was corrected for the background which was obtained by counting a blank solution processed in the similar manner as the sample solution.

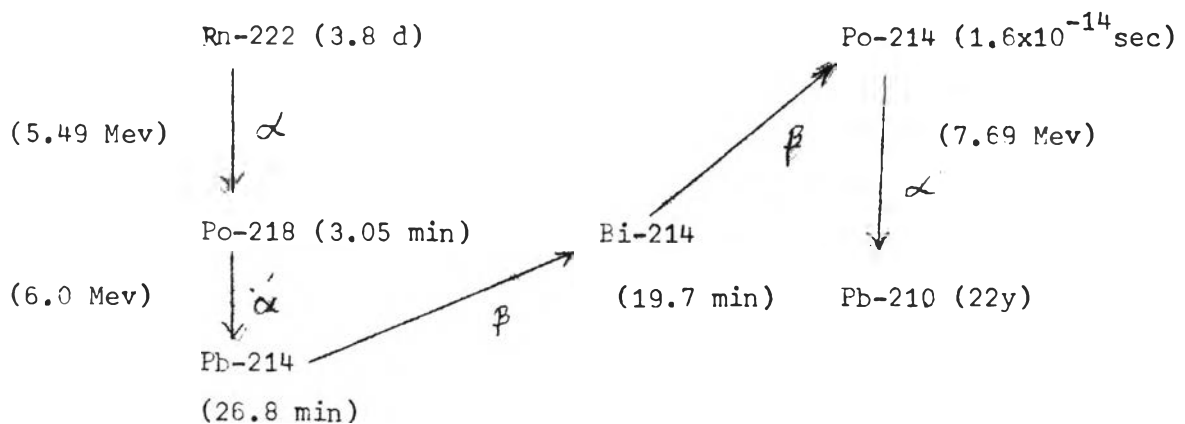
3.5 Determination of counting conditions.

For the determination of counting conditions, 19.6 cm^3 radium 226 solution containing 52.6 Pci cm^{-3} was added into a de-emanation flask. A portion of 6 cm^3 concentrated nitric acid and 300 cm^3 demineralised water was added to make the solution 0.3 mol/l in acidity. This standard solution was used to determine the gain and the discriminator

levels of the counter for radon measurement. Standard solutions of 10^4 and 111 Pci of radium-226 were used for the determination of the time for the establishment of equilibrium between radon and its daughters, and also the half-life of the de-emanation product respectively.

3.5.1 Determination of gain and discriminator settings.

The activity of radon and its daughters, polonium-218, lead 214, bismuth-214, polonium-214 and lead-210, were counted. The measurement involved three alpha particles and two beta particles. The decay scheme of radon-222 with energies of the emitted particles, is as follows: (17)



In order to obtain the optimal conditions for counting, the effects of gain and discrimination levels on count rate were studied. After second de-emanation, the vial was left for 3 hours before the radioactivity was counted by setting the lower discrimination level at 50 and the higher discrimination level at 1000. The gain was varied from 0.2 to 10 percent; the standard and the background were

counted for 4 minutes at each gain. The gain giving the maximum count rate was chosen as an optimum.

The gain of the counter was set at optimum and the discrimination levels were determined by setting a window width of 50 increments from 0 to 1000. The standard was counted for 4 minutes at each setting. The spectrum of radon and its daughters was obtained by plotting the count rate at each setting. The procedure was then repeated for background with a counting time of 20 minutes for each setting. The discrimination range that gives a maximum ratio of the square of efficiency to background (E^2/Bg) was selected. (17) The efficiency, E , could be calculated from the following equation:

$$E = \frac{c}{Ra f} \quad \text{cpmPci}^{-1}$$

where

- E = efficiency (cpmPci^{-1})
- c = count rate of radium-226 with an activity of Ra Pci after background correction (cpm)
- Ra = total activity of standard radium-226 (Pci)
- f = ingrowth factor = $1 - e^{-\lambda t}$
- λ = disintegration constant for radon
- t = ingrowth period

3.5.2 Determination of time required for establishment of radioactive equilibrium between radon and its daughters.

The time required for the establishment of radioactive equilibrium between radon and its daughters was determined by counting

the radon sample obtained from de-emanation at different time. The counting time for the sample and for the background were set at 20 minutes each. Measurement was continued after the radioactive equilibrium was established in order to obtain the decay curve of radon. The half-life of radon was confirmed from the decay curve.

3.6 Determination of optimum de-emanation conditions.

The effects on the carrier gas flow-rate, the de-emanation time, the particle size and the weight of silica gel as the radon-adsorber, the warm up time, the warm up temperature, the volume of liquid scintillator and the desorption temperature were investigated. A portion of 5 cm³ radium-226 solution containing 52.6 Pci cm⁻³ was added into a de-emanation flask. A portion of 6 cm³ concentrated nitric acid and 300 cm³ demineralised water was added to make the solution 0.3 mol/l in acidity. After first de-emanation, the sample was kept aside for radon ingrowth. Second de-emanation was performed at different conditions. The radon containing liquid scintillator was counted for 100 minutes and the efficiency (counts per minute per micro curie of radium-226 at equilibrium) was evaluated.

3.6.1 Effect of flow-rate of nitrogen gas and de-emanation time on efficiency.

In the study of the effect of the flow rate of nitrogen gas on the efficiency, the flow rates of nitrogen was varied between 100 and 400 cm³ min⁻¹. For each flow-rate, the times which required for de-emanation were varied to give a ratio of 5 to 30, with an increment

of 5, between the volume of nitrogen gas to the volume of the de-emanation solution. Two grams of silica gel with a particle size of 35-70 mesh was used as radon adsorber. The warm up time and the warm up temperature were 5 minutes and 0°C , respectively. The volume of the liquid scintillator was 15 cm^3 and the desorption temperature was 30°C .

3.6.2 Effect of particle size of silica gel on efficiency.

In order to obtain the optimum particle size of silica gel for the adsorption of radon, the fractions between 16-30 mesh, 35-70 mesh and 85-200 mesh were chosen and experimented. The weight of silica gel was fixed at 2 g, the flow rate of nitrogen was $150\text{ cm}^3\text{ min}^{-1}$ whereas the de-emanation time was 30 minutes. The warm up time and the warm up temperature were 5 minutes and 0°C respectively. The liquid scintillator volume was 15 cm^3 and the desorption temperature was 30°C .

3.6.3 Effect of weight of silica gel on efficiency.

The effect of the weight of silica gel on the efficiency was studied by varying the weight of silica gel between 1 and 3 g. The flow rate of nitrogen was $150\text{ cm}^3\text{ min}^{-1}$ and the de-emanation time was 30 minutes. The particle size of silica gel was 35-70 mesh, the warm up time was 5 minutes and the warm up temperature was 0°C . The liquid scintillator volume and the desorption temperature were 15 cm^3 and 30°C , respectively.

3.6.4 Effect of warm up time on efficiency.

The effect of warm up time on efficiency was studied by varying

the warm up time between 0 to 20 minutes. The flow rate of nitrogen and de-emanation time were $150 \text{ cm}^3 \text{ min}^{-1}$ and 30 minutes, respectively. Two grams of silica gel with a particle size between 35-70 mesh was used as the adsorber. The warm up temperature was 0°C whereas the liquid scintillator volume and the desorption temperature were 15 cm^3 and 30°C , respectively.

3.6.5 Effect of warm up temperature on efficiency.

In the investigation of the effect of warm up temperature, the warm up temperature was allowed to vary between 0°C and 50°C . The flow rate of nitrogen was $150 \text{ cm}^3 \text{ min}^{-1}$ and de-emanation time was 30 minutes. Two grams of 35-70 mesh silica gel was used as adsorber, the warm up time was fixed at 5 minutes. Fifteen cm^3 of liquid scintillator was used and the desorption temperature was 30°C .

3.6.6 Effect of volume of liquid scintillator on efficiency.

The optimum volume of liquid scintillator was determined by varying the volume between 10 and 18 cm^3 . The nitrogen flow rate and the de-emanation time were $150 \text{ cm}^3 \text{ min}^{-1}$ and 30 minutes, respectively. Two grams of silica gel with particle size between 35-70 mesh was used. The warm up time was 5 minutes whereas the warm up temperature was 0°C . The desorption temperature was 30°C .

3.6.7 Effect of desorption temperature on efficiency.

The temperature in which the vial was left during the time for the establishment of radioactive equilibrium between radon and its daughters or the desorption temperature, was studied by varying the

desorption temperature between 4 and 50 c. The flow rate of nitrogen was $150 \text{ cm}^3 \text{ min}^{-1}$ and the de-emanation time was fixed at 30 minutes. Two grams of silica gel with particle size between 35-70 mesh was used. The warm up time was 5 minutes whereas the warm up temperature was set at 0 c. The volume of the liquid scintillator was 15 cm^3 .

3.7 Determination of detection limit.

In the determination of the limit of detection, radium-226 activities between 0.5 and 728 Pci were pipetted into 300 cm^3 portions of 0.3 mol/l nitric acid solutions. After first de-emanation, the solutions were kept aside for radon-ingrowth. Second de-emanation was performed under optimal de-emanation conditions, and counted under optimal counting conditions. The efficiency, E, was evaluated for all solutions.

3.8 Quantitative analysis of radium-226 in ore samples.

3.8.1 Quantitative analysis of radium-226 in standard uranium ore sample

The solutions obtained from the digestion of the standard uranium ore sample prepared as described under section 3.3.1 were subjected to de-emanation under optimal conditions and subsequently counted under optimal counting conditions. The radium-226 content in the sample could be calculated from the following equation:

$$A = \frac{C}{E f M} \text{ Pci g}^{-1}$$

where

A = radium content in the sample (Pci g^{-1})

c = count rate of sample after background correction (cpm)

E = efficiency of the counting and de-emanation procedure,
obtained from known concentration of radium-226
solution. (cpm Pci^{-1})

f = ingrowth factor = $1 - e^{-\lambda t}$

λ = disintegration constant of radon

t = ingrowth time (day)

M = weight of sample (g)

3.8.2 Quantitative analysis of radium 226 in monazite samples.

The solutions obtained from the digestion of monazite samples prepared as described under section 3.3.2 were subjected to de-emanation under optimal condition and subsequently counted. The radium-226 content in the samples could be calculated in the similar manner as described under section 3.8.1