AN EASY METHOD FOR THE DETERMINATION OF RADIUM-226 USING LIQUID SCINTILLATION COUNTER

by

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Abstract

Radon-222 can be found in all environmental samples as a result of decay of Radium-226. When a sample solution of Radium-226 is mixed with an **organic** liquid scintillator, Radon-222 from decay of Radium-226 will be dissolved in a scintillator solvent and light is produced. The technique involves the introduction of 10 ml aliquot into a vial containing 5 ml liquid scintillator solution. The lower limit of detection (LLD) is 0.16 pCi/L at the 95 % confidence level. The method is probably rapid and simple and could be applied to both high and low activity of Radium-226.

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Introduction

Radium-226 (Ra-226) is a member of the uranium (4n+2) series and occurs in all uranium minerals. Pitchblende contains about 400 mg of radium per ton and uranium ores constitute the main sources of this isotope. Uranium occurs in nature as primordial elements in rocks so the Ra-226 is leached into water from rock and soil. The oceans contain about 20,000 tons of radium and the outermost miles of the earth's crust are estimated to contain about 1.3×10^7 tons of this isotope. Also, Ra-226 is absorbed from soil by food crops and is hence incorporated into the food chain of man (Ba 57; Se 66).

Ra-226 has a half-life of 1,620 years; it decays by alpha particles to radon-222, a noble gas with 3.84 days' half-life. The decay scheme of Ra-226 is shown in Figure 1. Ra-226 enters the body by intake of contaminated food and water. Because of its similarity in metabolic behavior to calcium, Ra-226 is deposited in bone and is eliminated very slowly and induces bone sarcomas and carcinomas in soft tissues abjacent to bone (Se 66). As Ra-226 decays to Rn-222, an alpha emitter, the accumulation of Rn-222 gas in the head cavities is the major inducer of head carcinomas (Mays 85).

The 1976 Environmental Protection Agency Interim Primary Drinking Water Regulations established a maximum contaminant level for Ra-226 of 3 pCi/L (APHA 80). The International Commission on Radiological Protection and the National Committee on Radiation Protection have specified the maximum amount of Ra-226 that may be tolerated when fixed in the body for long periods of time is 0.1 uCi. The air concentration that will result in this amount being fixed is 10^{-11} uCi/cm^3, if contaminated air is breathed continuously (Se 66).

Ra-226 has been mainly used in medicine for gamma-ray therapy (e.g., for the treatment of cancer); the gamma radiation is emitted by some of the Rn-222 daughters. Rn-222 is often used separately in tiny ampoules or seeds for irradiation of tissues. Ra-226, and to a lesser extent Rn-222, have been used in industrial gamma-ray radiography to detect flaws in casting, and for thickness measurements. A small amount of Ra-226 is used for the production of self-luminous paints in conjunction with scintillators such as zinc sulfide. Mixtures of radium salts and beryllium have been used for neutron sources (Ba 57, Se 66).

The determination of Ra-226 depends on types and concentration of sample. Ra-226 may be detected by gamma-ray spectrometry when present in sufficiently high quantity. In small amounts, such as in water, soil, food, and biological samples, radium measurement requires chemical separation and purification. Present methods used include co-precipitat with barium nitrate or barium chloride, ion exchange in resin column, an solvent extraction. Detection by emanation method is the most widely us technique. Liquid scintillation technique presented in this report is developed for analysis of Ra-226 with high accuracy, automatic sample changing, and a good detection limit.

Principle

Rn-222 is generally more soluble in organic solvent than in water. When a sample solution of Ra-226 is mixed with an organic liquid scintillator, Rn-222 from decayed Ra-226 will be dissolved in a scintillator solvent and light is produced. The flashes of light are detected and amplified by one or more photomultiplier tubes. The ingrowth of alpha activity from Ra-226 increases at a rate governed

primarily by Rn-222. From the decay series (Fig. 1), it is shown that the alpha activity grows into separated Ra-226 with the half-life of Rn-222, and the growth reaches equilibrium within 30 days, at which time the total alpha activity is four times the initial activity (APHA 80, Se 66). The counting technique has been described in detail by Prichard and Gesell (Pr 77).

Methodology

A. Apparatus

Liquid scintillation counter

20-ml syringe

18-gauge, 2-inch hypodermic needles

Glass scintillation vial

B. Reagent--mineral oil base scintillator

C. Procedures

1. Use the syringe to draw 12-15 ml of sample solution.

2. Eject any small air bubbles and extra water, retain precisely 10 ml of sample solution in the syringe.

3. Transfer the sample solution from the syringe to a vial containing 5 ml liquid scintillator solution.

4. Seal and store for three weeks to allow the radon to reach equilibrium with Ra-226.

5. Prepare a calibration curve using Ra-226 standard solution with activities ranging from 0.63 to 15.00 pCi/vial.

6. Determine the background by counting vials containing distilled water and scintillator prepared in the same way as the sample. Use one liter of distilled water and preconcentrate by evaporating on the hotplate until the volume is equal to 10 ml. Then the 10 ml of distilled water represents one liter.

Results

The ingrowth curve of radon and the calibration curve are shown in Figures 2 and 3 and the data for these plots are summarized in Tables 1 and 2, respectively.

The lower limit of detection (LLD), blank value plus three times standard deviation, for a 40 minute count and 10 ml distilled water was determined to be 0.16 pCi/L. The reproducibility was determined by replicate measurements. The accuracy of measurements was determined by analysis of the U.S. EPA cross-check samples. The results of reproducibility and accuracy measurements are shown in Table 3.

Discussion and Conclusions

The method is probably rapid and simple by drawing the 10 ml aliquot into a syringe and then transferring the aliquot to a liquid scintillation vial which contains the mineral-oil based scintillation solution. The volume of sample must be measured precisely and the use of contaminated glassware should be avoided.

An Ra-226 standard and two cross-check samples from U.S. EPA quality assurance program were used to evaluate the method. The results of this evaluation showed that this is a highly reproducible and accurate method. The lower limit of detection (LLD) is 0.16 pCi/L at the 95% confidence level. The ingrowth curve in Figure 2 shows that in three weeks of storage, Rn-222 in the samples reaches equilibrium with Ra-226. A counting time of a least 40 minutes is recommended.

For samples that contain high concentrations of Ra-226, direct measurement in 10 ml of water can be done. However, the Ra-226 content of natural water is often low, so the preconcentration step and the radiochemical separation are needed. From the preliminary experiments

it was found that preconcentration by evaporation results in samples with high dissolved solids and strong coloration of the solution, which reduces the counting efficiency. Therefore, preconcentration alone is not suitable for liquid scintillation counting.

After preconcentration, co-precipitation of radium with barium as $Ra(Ba)SO_4$ should be carried out. The precipitate is then dissolved in alkaline EDTA solution, mixed with liquid scintillator solution, and then counted. The results show that these two steps, preconcentration and purification, are practicable and efficient.

Table 1. Data for ingrowth curve, suitable time period in storing sample using 187.5 pCi Ra^{226} concentrations/vial.

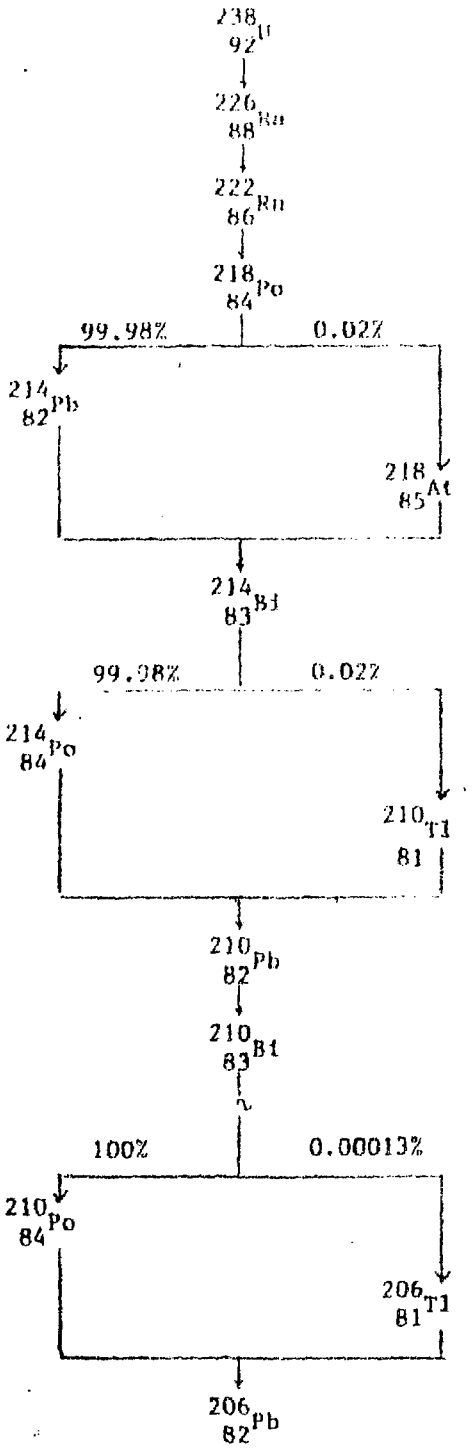
Days	cpm
1	9.58
2	53.27
5	148.62
9	340.14
12	658.45
16	987.77
18	1006.25
22	1150.77
24	1157.15
30	1167.50

Table 2. Radium-226 count rate in minutes (cpm) for calibration curve.

Concentration pCi/10 ml	Count rate cpm
0.68	1.98
1.35	4.61
2.03	7.32
2.70	10.20
3.75	13.56
5.63	20.26
7.50	26.16
9.38	34.11
11.25	41.00
15.00	54.01

Table 3. Reproducibility and accuracy test using spiked sample and intercomparison sample from U.S. EPA.

Number of test	Result (pCi/L)
Spiked Sample	
1	15.25
2	14.89
3	15.00
4	15.56
5	14.69
Average value	15.07 ± 0.34
Known value	15.00
U.S. EPA	
1	6.50
2	6.26
3	5.62
Average value	6.13 ± 0.45
Known value	6.10 ± 0.92
1	6.60
2	6.42
3	6.65
Average value	6.56 ± 0.12
Known value	6.30 ± 0.95



Uranium I	4.51×10^9 years
Radium	1,620 years
Radon	3.82 days
Radium A	3.05 min
Radium B	26.8 min
Astatine	~ 2 sec
Radium C	19.7 min
Radium C'	164 μsec
Radium C''	1.3 min
Radium D	21 years
Radium E	5.01 days
Radium F	138.4 days
Radium E''	4.19 min
Radium G	Stable

Fig. 1. The uranium (4n+2) series.

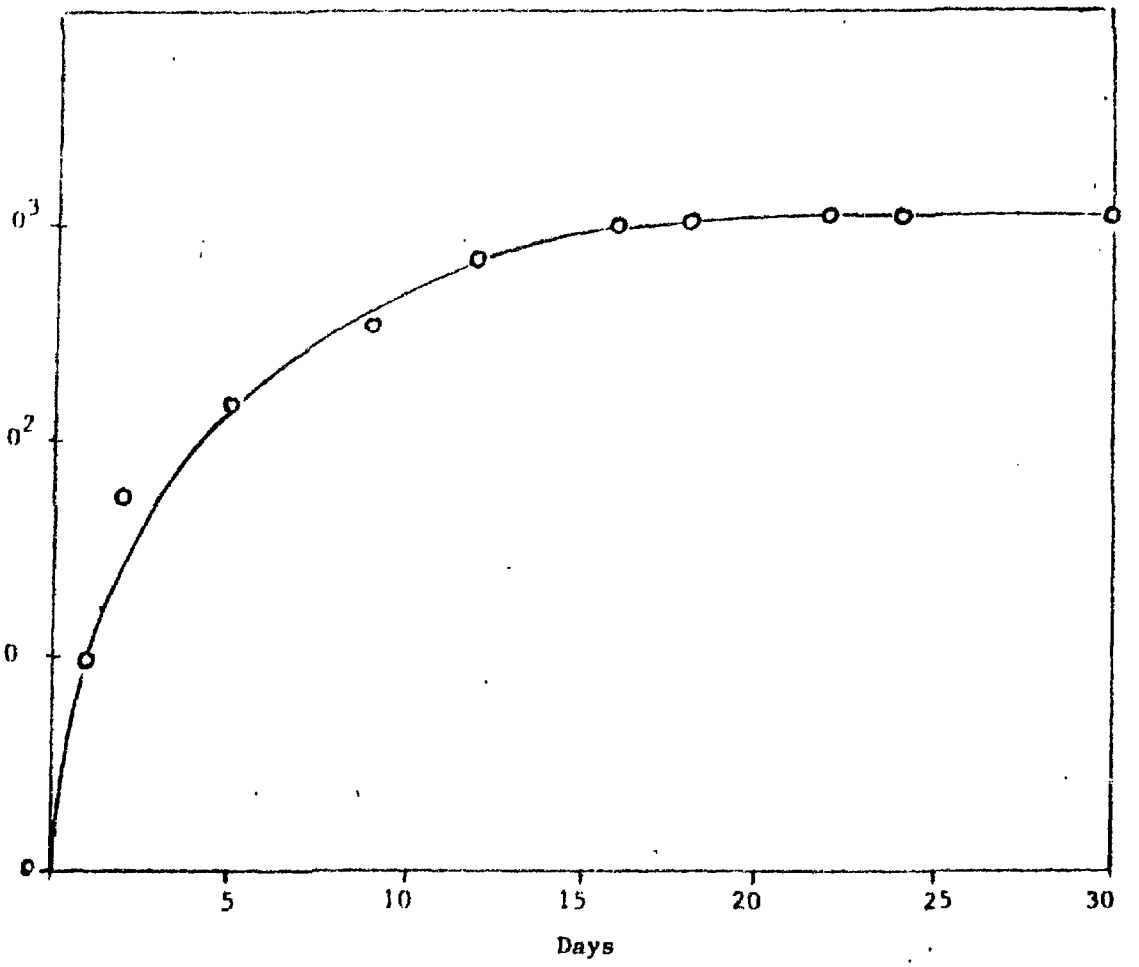


Fig. 2. Ingrowth curve of Rn-222 from Ra-226 in the scintillation vial.

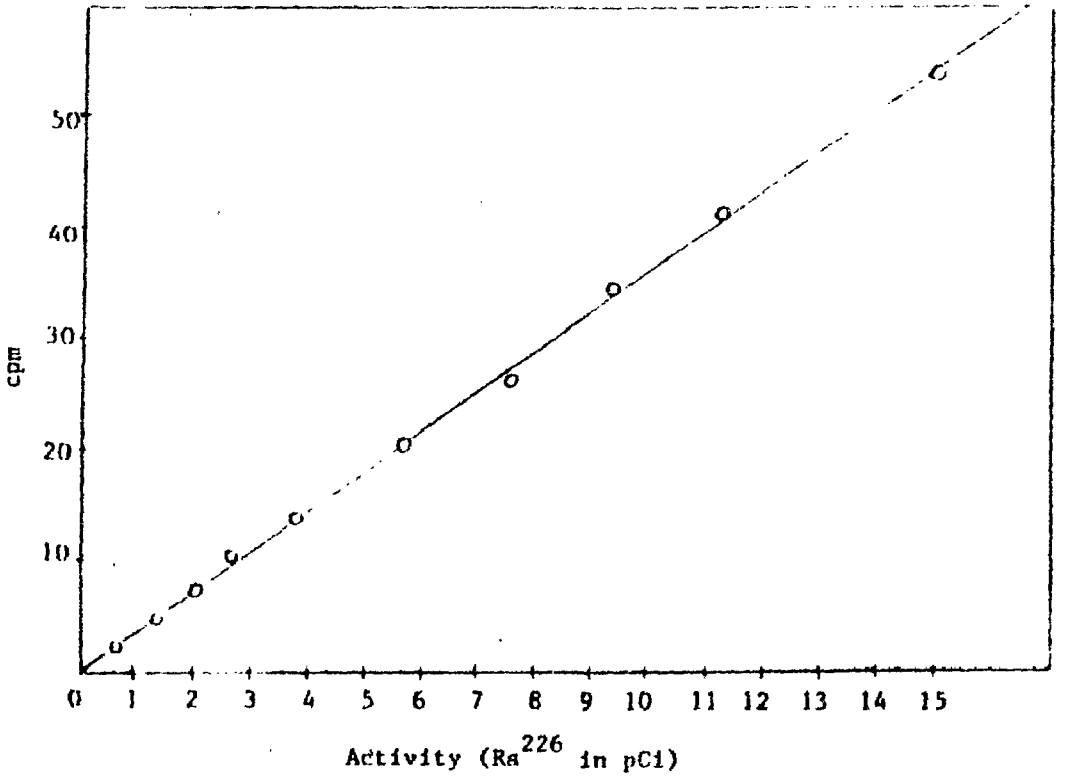


Fig. 3. Calibration curve of Ra-226 counted in liquid scintillation counter.

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