Radon emanometric technique for ^{226}Ra estimation

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Abstract Studies on natural background radiation show that the major contribution of radiation dose received by population is through inhalation pathway vis-à-vis contribution from radon (^{222}Rn) gas. The immediate parent of radon being radium (^{226}Ra), it is imperative that radium content is measured in the various matrices that are present in the environment. Among the various methods available for the measurement of radium, gamma spectrometry and radiochemical method are the two extensively used measurement methods. In comparison with these two methods, the radon emanometric technique, described here, is a simple and convenient method. The paper gives details of sample processing, radon bubbler, Lucas cell and the methodology used in the emanometric method. Comparison of emanometric method with gamma spectrometry has also undertaken and the results for a few soil samples are given. The results show a fairly good agreement among the two methods.

Keywords Radium estimation · Emanometry · Lucas cell

Introduction

Considerable interest in the behaviour of the natural radionuclides of uranium and thorium and their daughter products in the terrestrial environment were shown by

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scientists for the past few decades [8]. Further interest in the behaviour of these elements in soils is linked with the potential environmental problems associated with extracting and processing material containing naturally occurring radioactive materials (NORM). Apart from U industry, the major wide-spread contributor to environmental radioactivity is phosphate and fly ash industries. Interest in the environmental behaviour of radium follows from its ubiquitous presence of NORM [14]. There are four radium isotopes in the natural environment. These are α-emitting ^{226}Ra ($T_{1/2}$ = 1,600 years) in the uranium series, α-emitting ^{223}Ra ($T_{1/2}$ = 11.43 days) in the actinium series and β-emitting ^{228}Ra ($T_{1/2}$ = 5.75 years) and α-emitting ^{224}Ra ($T_{1/2}$ = 3.66 days) in the thorium series. Radium isotopes are most dangerous natural radionuclides, because (i) following their decay a number of other alpha producing short lived daughter nuclides are produced and (ii) radium is easily incorporated in the bones of mammals due to their chemical and biological behavior, similar to that of other alkaline earth metals (Ca, Sr, Ba) and can cause enhanced radiation dose to man [4]. Therefore the determination of radium in soil is important in view of human health, environmental risk and geochemical studies, specially related to uranium. In environmental surveys, a procedure is required for assessing the ^{226}Ra from the soil samples combining specificity and sensitivity with minimal sample preparation [9]. Among the isotopes of radium present in nature, only alpha emitting isotopes are of significance in view of health effects and their short lived isotopes ^{223}Ra and ^{224}Ra are not of much concern considering the long term effects. Hence, the methodology developed in this work is specific to ^{226}Ra estimation in various sample matrices. Gamma spectrometry and radiochemical separation are the two commonly used methods followed for the estimation of ^{226}Ra. In gamma spectrometry, ^{226}Ra is

estimated through [222]Rn after it attains equilibrium with [226]Ra in the sample. In this method, the sample is sealed air tight and preserved for over 30 days for attaining equilibrium between [222]Rn and [226]Ra before the sample is taken for counting. Moreover, in gamma spectrometry, the detection efficiency being low, large quantity (~ 500 g) of sample is required for analysis. In radiochemical analysis, radium is chemically separated and counted through its alpha activity. In this method, the chemical processes involved in separating radium from the sample matrix are quite tedious and cumbersome. Emanometric technique described in this work, for the estimation of [226]Ra, is simple in respect of sample processing compared to radiochemical separation method and rapid as compared to gamma spectrometric technique. In the present study few soil samples were analyzed for [226]Ra by emanometric as well as γ-spectrometry methods. A comparative study has been made from the results obtained by the two methods with respect to precision and accuracy of the results.

Experimental details

Preparation of soil samples

Soil samples were collected from selected sampling locations following the protocols specified by US EPA sampling procedure. The samples were dried in an oven at 110 °C for 8–10 h for removing moisture. The samples were then powdered, sieved and taken for leaching. Known quantity of the sample (normally 5–10 g) was weighed accurately and 50–100 mL of conc. HNO_3 was added to the sample and heated on a hot plate. Small quantity of H_2O_2 was added to the mixture carefully to remove organic matter present in the sample. Acid leaching was done repeatedly for three times and the mixture was filtered and made up to volume (100 or 200 mL). The resultant acid normality of the sample was maintained at 4 N. Samples leached in HNO_3–H_2O_2 mixture are found to have more than 98% dissolution for radium from various sample matrices [7]. However, for complete dissolution of radium from soil samples, silica removal with HF treatment is recommended.

The Lucas cell

The Lucas scintillation cell (LSC) is commonly used all over the world for estimation of radon. The cell was originally devised by Vandilla and Taysum [15]. The cell has been modified since by others [1, 5, 6, 10, 11]. Air sample is taken inside the Lucas cell through an online filter by vacuum collection. The concentration of radon is evaluated using the efficiency factor for the counting system and from the theoretical factors computed for the decay of radon inside the
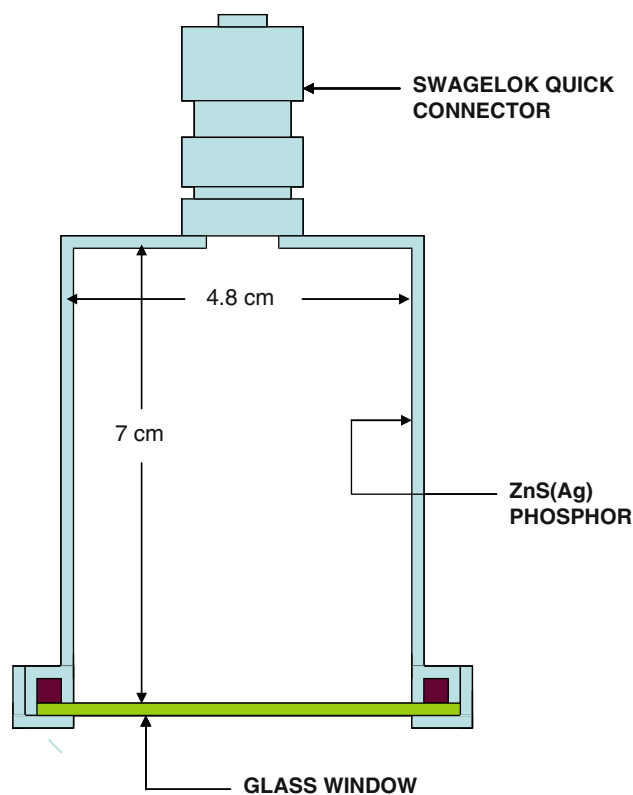

Fig. 1 Schematic diagram of the Lucas cell

Lucas cell and for the build up of radon decay products with respect to sampling and counting delays [2]. The principle of detection is counting of photons resulting from the interaction of alpha particles due to radon and its progeny with the ZnS (Ag) scintillator. A photomultiplier (PM) tube assembly counts the photon events. Figure 1 gives the schematic diagram of a Lucas cell.

Methodology

An aliquot of the sample (normally 50 mL) is transferred into the radon bubbler. The sample is degassed by bubbling filtered air through the sample solution to remove radon already present in the bubbler. The bubbler is sealed at both the ends and allowing the radon to build up inside the sample solution. The time of sealing is noted and sampling of the gas from the bubbler is done after a delay time depending on the expected [226]Ra activity of the sample. The activity build up of [222]Rn from its parent [226]Ra is calculated for the period from sealing time to the sampling time using radioactive build up formula. The radon gas built up inside the bubbler, is totally transferred into an evacuated Lucas cell that was already counted for its background alpha counts. After a delay of more than 200 min post sampling, time required for the progeny nuclides to attains equilibrium with radon inside the Lucas

cell, the Lucas cell was coupled to an alpha counting system and counted. The net counts for the counting period (total counts − background counts) are recorded for the sample and computed for radium activity in the Lucas cell using Eq. 1 (See Appendix 1 for theoretical computation.)

$$^{226}\text{Ra(Bq)} = \frac{6.967 \times 10^{-5} \times C}{Ee^{-\lambda t}(1 - e^{-\lambda t})(1 - e^{-\lambda \theta})} \quad (1)$$

where, C = Net counts above background for counting period 'T', 6.967×10^{-5} = product of some constants and λ of radon (s^{-1}), t = counting delay (min), E = efficiency of the counting system (71%), T = counting duration (min), θ = Radon build up period in the bubbler (min), λ = Decay constant of radon (min^{-1}).

Once ^{226}Ra activity (Bq) is estimated in the volume of sample taken, activity per kg of soil is computed using Eq. 2

$$^{226}\text{Ra(Bq/kg)} = \frac{^{226}\text{Ra(Bq)} \times V_O \times 10^3}{M \times V_A} \quad (2)$$

where, 'M' = Weight of the sample taken for leaching (g), V_O = Volume made up of the sample (mL), V_A = Volume of the sample taken for analysis (mL).

An uncertainty in this method is possible if ^{220}Rn is also sampled into the Lucas cell from sample solution. The presence of ^{224}Ra, a natural radionuclide form ^{232}Th series, in the sample can also get dissolved during the acid leach process and can build up ^{220}Rn inside the radon bubbler. However, when samples are from background areas or from uranium deposited areas, other than thorium enriched locations, the alpha counts contributed due to ^{220}Rn progenies are negligible. In any case the contribution from ^{220}Rn can be estimated in the sample by a delay counting technique after the Lucas is degassed for ^{222}Rn + ^{220}Rn collected. After the first counting is over, the cell is degassed and allowed to remain for another 200 min for the ^{222}Rn progenies to decay inside the cell. ^{212}Pb, the progeny nuclide from ^{220}Rn, with a half life of 10.6 h will govern the immediate alpha decay of the progenies ^{212}Bi and ^{212}Po. Now the cell is counted for alpha activity for a suitable period. By applying the decay correction from the time of sampling to second counting, average count rate due to ^{212}Pb daughter nuclides (^{212}Bi and ^{212}Po) can be obtained. For a precise calculation the activity build up factor for ^{212}Bi atoms (36%) from sampling time to start of first counting can be applied, if the first counting is carried out before equilibrium between ^{212}Pb and ^{212}Bi is attained. For high concentrations of ^{222}Rn and ^{220}Rn in a sample one can follow the method followed by Eappen et al. [3] for the simultaneous measurements of radon and thoron in the samples.

The minimum detection level for various counting durations are computed and presented in Fig. 2. The figure indicates that for a background count of 6 cph at 71% counting efficiency, the MDL could be brought down to
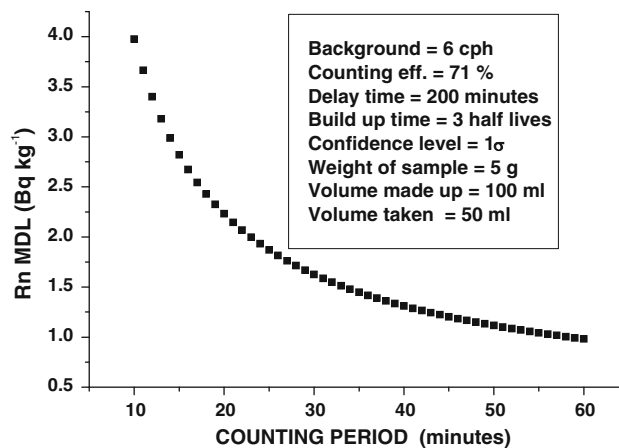

Fig. 2 MDL calculation for radon by Lucas cell

1 Bq/kg with a confidence level at 1σ, when the counting period is increased to 60 min. In this case the sample weight is 5 g made up to 100 and 50 mL is taken for analysis. Also the radon build up time is taken as 3 half lives (11.5 days) and delay for start of counting from sampling time is taken as 200 min.

Radionuclide analysis by gamma-ray spectrometry:

The soil samples estimated for ^{226}Ra by emanometry were also analyzed for ^{226}Ra by gamma spectrometry. A high resolution gamma spectrometer using HpGe detector with data analysis method given by [12, 13] was used for the analysis. The detector has 30% relative efficiency with respect to 3″ × 3″ NaI(Tl) detector and an energy resolution of 1.8 keV for 1.33 meV gamma photons from a point source of ^{60}Co at 25 cm height with a 2% uncertainty in counting. Samples were dried in an oven at 110 °C overnight to remove moisture. About 350 g of soil samples were filled and sealed in leak proof cylindrical plastic containers of 6.5 cm diameter and 7.5 cm height for a period of 1 month so as to attain secular equilibrium between ^{226}Ra, ^{222}Rn and its daughter nuclides prior to analysis by gamma spectrometry. Energy peaks used for estimation of ^{226}Ra were 186.1 keV from ^{226}Ra, 609.4 and 1,764.5 keV from ^{214}Bi. The overall error in estimation is calculated to be around 15%. The results are presented in Table 2.

Results and discussion

Table 1 gives the results of soil samples for ^{226}Ra analysis by emanometric technique and Table 2 gives the comparison between emanometric and gamma spectrometry. Comparison between gamma spectrometry and emanometric method showed very close proximity in their results. Correlation graph (Fig. 3) gives a correlation coefficient

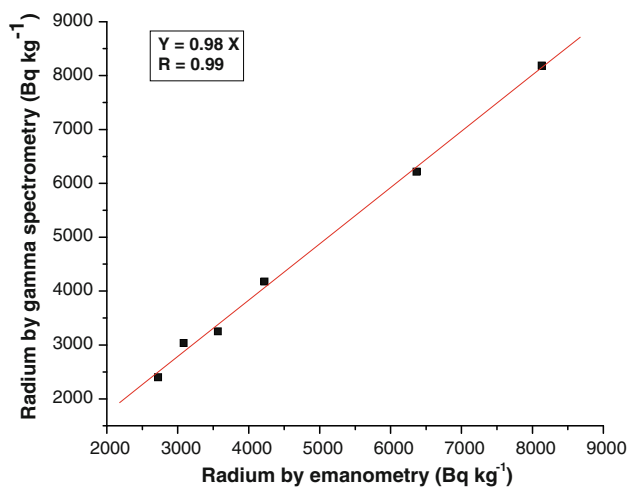**Table 1** Results of ^{226}Ra (Bq/kg) obtained from the soil samples by emanometric technique

Sample no.	Net counts	Counting delay t (min)	Counting duration T (min)	Radon build-up period θ (min)	Weight of sample M (g)	Vol. made up V_O (mL)	Vol. taken V_A (mL)	^{226}Ra (Bq/kg)
JM-01	16092	248	10	13118	5.1645	100	50	6216 ± 49
JM-02	21018	253	10	13112	5.1258	100	50	8187 ± 56
JM-03	16218	228	20	12974	5.3440	100	50	3034 ± 24
JM-04	36939	61	30	18866	5.1271	100	50	4178 ± 22
JM-05	6131	243	10	13101	5.0925	100	50	2400 ± 31
JM-06	16698	235	20	13070	5.1203	100	50	3254 ± 25

± Value indicates the error associated with the measurements

Table 2 ^{226}Ra (Bq/kg) obtained from emanometry and gamma spectrometry

Sl no.	Location no.	^{226}Ra by emanometric analysis (Bq/kg)	^{226}Ra by gamma spectrometry (Bq/kg)
1	JM-01	6216 ± 49	6367 ± 38
2	JM-02	8187 ± 56	8132 ± 22
3	JM-03	3034 ± 24	3084 ± 41
4	JM-04	4178 ± 22	4222 ± 25
5	JM-05	2400 ± 31	2722 ± 19
6	JM-06	3254 ± 25	3567 ± 29

± Value indicates the error associated with the measurements

Fig. 3 Correlation graph between gamma spectrometry and emanometry

close to one indicating the closeness among the two methods. The slope of 0.98, indicating a lower result for the emanometric compared to gamma spectrometry can only be attributed to instrumental incompatibility (in terms of measurement efficiency) among the two methods.

Conclusions

Results show that the emanometric method can be conveniently used for the various types of samples in determining radium content in them. The major advantages for the method are (i) lower detection level (ii) requirement of minimum quantity of sample and (iii) least estimation time. Comparison of results obtained from emanometric method with gamma spectrometry shows that the method is correct and can be used for various types of samples. Samples with higher concentrations of radium can be analyzed in short duration by reducing the build-up time after degassing.

Appendix 1

Theoretical model for computing radium activity by emanometry

Figure 4 gives the decay series of radium, radon and short lived progeny nuclides. Let $(N_1)_0$ be the number of radon atoms in the bubbler volume at sampling time (call it as 'zero time'). Let the number of atoms of ^{222}Rn, ^{218}Po, ^{214}Pb and ^{214}Bi at any subsequent instant be N_1, N_2, N_3 and N_4 respectively and let the corresponding decay constants
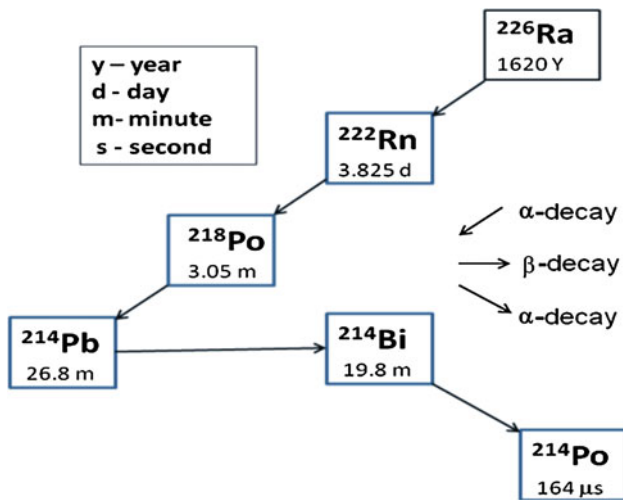
Fig. 4 Decay series of radium-radon and short lived daughter products

be λ_1, λ_2, λ_3 and λ_4. Let $A(t)$ be the total number of alpha particles emitted from the composite sample of radon and progeny nuclides from instant zero to time t. If the total number of alpha particles emitted by radon, ^{218}Po, ^{214}Pb and ^{214}Bi (i.e. ^{218}Po) during the same interval (i.e. 0–t) are $A(t)_1$, $A(t)_2$ and $A(t)_4$ then

$$A(t) = A(t)_1 + A(t)_2 + A(t)_4. \tag{3}$$

Since the radon activity at any instant is $N_1\lambda_1$, it can be shown that

$$A(t)_1 = (N_1)_0 [1 - e^{\lambda_1 t}]. \tag{4}$$

Similarly it can be shown that

$$A(t)_n = (N_1)_0 \sum_{i=1}^{n} \frac{\Pi_{j=1 \neq j}^{n} \lambda_j}{\Pi_{j=1 \neq j}^{n} \lambda_j - \lambda_i} [1 - e^{-\lambda_i t}] 0 \tag{5}$$

From Eq. 5 Eq. 3 can be generated. Substituting the numerical values for the decay constants Eq. 3 may be rewritten as:

$$A(t) = (N_1)_0 \Big[K_1\big(1 - e^{-\lambda_1 t}\big) + K_2\big(1 - e^{-\lambda_2 t}\big) + K_3\big(1 - e^{-\lambda_3 t}\big) + K_4\big(1 - e^{-\lambda_4 t}\big) \Big], \tag{6}$$

where $K_1 = 3.00978$, $K_2 = -0.00074$, $K_3 = -0.02094$ and $K_4 = 0.01180$. When counting starts beyond a delay of 180 min, Eq. 6 gets simplified because the the exponential terms involving the decay constants of the daughter products can be considered zero. Thus the equation is simplified as:

$$A(t) = (N_1)_0 \big[K_1\big(1 - e^{-\lambda_1 t}\big) + K_2 + K_3 + K_4 \big] \tag{7}$$

For values of $t \geq 180$ min.

From Eq. 7 the total number of alpha particles emitted by radon and its daughters during counting interval of 'T' min starting from a delay time 't_1' post sampling to delay

time 't_2' i.e. end of counting time ($t_2 - t_1 = T$) can be calculated as:

$$\alpha = \alpha_{t_2} - \alpha_{t_1} = (N_1)_0 K_1 \big[\big(1 - e^{-\lambda_1 t_2}\big) - \big(1 - e^{-\lambda_1 t_1}\big) \big]$$
$$= (N_1)_0 K_1 \big[\big(1 - e^{-\lambda_1(t_1+T)}\big) - \big(1 - e^{-\lambda_1 t_1}\big) \big]. \tag{8}$$

Let the net counts obtained during the counting 'T' be 'C' and counting efficiency be 'E' percent. Suppose the number of atoms of radon in the cell at the time of sampling from the bubbler is $(N_1)_0$ corresponding to a concentration of R (Bq) then 'C' and 'R' can be equated as:

$$C = \alpha \frac{E}{100} = \frac{(N_1)_0 K_1 E \big[\big(1 - e^{-\lambda_1(t_1+T)}\big) - \big(1 - e^{-\lambda_1 t_1}\big) \big]}{100} \tag{9}$$

$$(N_1)_0 = \frac{100 \times C}{K_1 E[(1 - e^{-\lambda_1(t_1+T)}) - (1 - e^{-\lambda_1 t_1})]} \tag{10}$$

$$R(\text{Bq}) = (N_1)_0 \lambda_1 = \frac{100 \times \lambda_1 C}{K_1 E[(1 - e^{-\lambda_1(t_1+T)}) - (1 - e^{-\lambda_1 t_1})]}. \tag{11}$$

When counting delay and counting duration is taken in minutes and replaced K_1 and λ_1 (min^{-1}) Eq. 11 is simplified as:

$$R(\text{Bq}) = \frac{6.967 \times 10^{-5} \times C}{E e^{-\lambda t}(1 - e^{-\lambda t})}. \tag{12}$$

Activity of radium in the bubbler is calculated after applying the radon build up factor in Eq. 12 where θ is the buildup period for radon inside the bubbler

$$^{226}\text{Ra(Bq)} = \frac{6.967 \times 10^{-5} \times C}{E e^{-\lambda t}(1 - e^{-\lambda t})(1 - e^{-\lambda \theta})}. \tag{13}$$

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