HIROSAKI UNIVERSITY

Radiation Environment and Medicine 2018 Vol.7, No.1 53–57

REM
Radiat Environ Med

Note

Selection of Reference Method for Thoron Measurements Performed for Calibration of CR-39 Based SSNTDs

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Received 30 August 2017; revised 19 October 2017; accepted 23 November 2017

For the accurate calibration of CR-39 based SSNTDs, a protocol shall be given which contains parameters of the calibration chamber as well as the calibration and reference method. The specification of the reference method is an important task. During this work various gamma spectrometric and scintillation techniques capable for thoron measurement were tested in the interest of selecting a reference method for the validation of thoron calibration. Comparison measurements were performed in the calibration chamber with the suitable techniques and the available active devices. Based on the results, scintillation counting according to two counts method has been proposed as reference method for thoron measurements.

Key words: thoron measurement, reference method, thoron calibration, scintillation, gamma spectrometry

1. Introduction

Previous surveys indicate that the accurate determination of thoron concentration is important for several reasons[1-6]. During protracted campaigns, the application of active devices is not feasible. Therefore, integral devices, such as solid state nuclear track detectors (SSNTDs), are commonly used[7-11]. The application of track detectors requires a well-defined calibration method. The technical difficulties concerning measurement due to the short half-life make development of a calibration chamber and its validation complicated. Recently, a thoron calibration chamber has been developed at the Institute of Radiochemistry and Radioecology (RRI) at the University of Pannonia; however, our experience suggests further development is necessary for increased accuracy[12]. Furthermore, a protocol shall be given for the calibration process, containing parameters of the calibration chamber and the methods for calibration and validation.

The specification of the reference method is an important task for a calibration protocol. The goal of this research is to choose a reference instrument or technique for the verification of the results from other instruments or techniques. For this purpose, selection of a method based a simple physical principle with relatively low uncertainty is advisable, which can be considered as a first reference; therefore, the results of the measurement can be easily traced back to SI units. For thoron measurements, scintillation counting[13] or gamma spectrometry[14] could be suitable. These methods can be validated with the measurement of a validated radon source available in our institute, as a reference etalon. In case of more complicated active monitors, where usually semi-conductor detectors are applied, the validation could not be performed directly.

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Among scintillation counters, Lucas cells are commonly used for thoron measurements[13, 15-18]. Different techniques are able to measure thoron and radon activity simultaneously[15-16, 19]. After a literature survey selected scintillation techniques were examined and compared to the available thoron measuring instruments.

The gamma spectrometric experiments were based on the method described by Gargioni *et al.*[20]. According to this, a ^{228}Th source made by electrodeposition is placed into a chamber which is placed onto gamma spectrometer with high purity germanium (HPGe) detector. The chamber is connected to a space with known volume and the generated thoron gas is carried into this space by a pump. Thereby, thoron gas exhaled from the source is continuously deprived from the chamber; therefore, secular equilibrium between ^{224}Ra and ^{212}Pb is disrupted and after a time ^{212}Pb activity decreases (half-life of ^{212}Pb is 10.6 hours). The thoron's remaining ^{212}Pb activity remains in the source (not-exhaled), thus the activity decrease is proportional with the emanation. Emanation is calculated from the remaining ^{212}Pb and ^{224}Ra activity (equal to ^{228}Th activity due to secular equilibrium).

Based on the results, a proposal has been given for the potential reference technique.

2. Material and methods

2.1. Scintillation techniques

During the experiments, a modified two counts method (TCM) and an integral method were applied[15].

In case of TCM, a Pylon AB-5 counter and Pylon 300A Lucas cell (Pylon Electronics Inc., Canada) were used. The process was performed as it follows:

1. Pulse counting during the interval of 20 – 120 s after sampling;
2. Pulse counting during the interval of 600 – 900 s after sampling.

Thoron and radon activity were calculated from the counts registered during the two counting periods.

Pulses registered during the second period come from the activity of radon as well as the ^{218}Po and ^{214}Po activity generated from the decay. The time dependency of the activity can be described by Equation 1:

$$\frac{dA_{Rn-222}}{dt} = A^{o}_{Rn-222}\ e^{-\lambda_{Rn-222}t} \quad (1)$$

This equation is solved by integration between the borders of the second measuring period (t_3 and t_4). From this and the previous approach, the initial radon activity (in the moment of t = 0), which equals the radon activity of the sampled media, is calculated by Equation 2:

$$A_{Rn-222} = \lambda_{Rn-222}\frac{I_{2,N}}{(\eta_{Rn-222}+\varepsilon_2\eta_{Po-218})(e^{-\lambda_{Rn-222}t_3}-e^{-\lambda_{Rn-222}t_4})} \quad (2)$$

where $I_{2,N}$ is the net pulse value registered during the second measuring period, λ_i the decay constant of the i radionuclide, η_i is the counting efficiency of the scintillation cell for the i radionuclide and ε_2 represents the equilibrium between ^{222}Rn and ^{218}Po for the second measuring period. For simplification, it can be calculated for the arithmetic mean of the measuring interval ($\bar{t}_2$) from Equation 3:

$$\varepsilon_2 = 1 - e^{\bar{t}_2(\lambda_{Rn-222}-\lambda_{Po-218})} \quad (3)$$

Similarly, the thoron activity can be calculated from Equation 4:

$$A_{Rn-220} = \lambda_{Rn-220}\frac{I_{2,N}-A_{Rn-222}(\eta_{Rn-222}-\varepsilon_1\eta_{Po-218})}{(\eta_{Rn-220}+\eta_{Po-216})(e^{-\lambda_{Rn-220}t_1}-e^{-\lambda_{Rn-220}t_2})} \quad (4)$$

where $I_{1,N}$ is the net pulse value registered during the second measuring period and ε_1 represents the equilibrium between ^{222}Rn and ^{218}Po for the first measuring period.

In case of the integral method, NDI intelligent scintillation detector with Lucas cell (Gamma Technical Corporation, Hungary) was applied. Counts were registered for 1000 s with 1 s integration time. Thoron concentration was calculated from the decay equation. Measurements with NDI system were also performed according to TCM method for comparison.

Measurements were performed to compare the mentioned scintillation techniques and the available active radon/thoron monitors such as Sarad EQF 3220, Sarad RTM 2100 (Sarad GmbH, Germany) and Durridge RAD7 (Durridge Company Inc., USA).

The comparison measurements were performed using thoron chamber at the Institute of Radiochemistry and Radioecology. The standard calibration setup was applied: an external thoron source was connected to the chamber to produce ca. 20 000 Bq m^{-3} thoron concentration inside and circulation was provided by a pump with a 4 L min^{-1} flowrate. During sampling, an evacuated Lucas cell was connected to the chamber, and the thoron gas was sucked in by vacuum after opening the valve. The measuring period was 4 days; sampling was performed three times a day in two hour intervals.

2.2. Gamma spectrometry

These experiments were performed based on the method described by Gargioni *et al.*[20]. In the experiments, ceramic source samples were used instead of an electrodeposition source. The sample was placed in an accumulation chamber. The internal measuring chamber of a Sarad EQF 3220 was used as a reference volume, and the internal pump of the instrument was used to deprive thoron gas from the accumulation chamber. The ^{212}Pb

and the ^{224}Ra activities in the accumulation chamber were measured by an Ortec GMX40-76 HPGe detector. The 239 keV gamma line of ^{212}Pb and the 241 keV gamma line of ^{224}Ra were used, which are separable by a high resolution HPGe detector. The efficiency of the detector is neglected due to the relatively close energies.

The emanation coefficient is calculated from Equation 5[20]:

$$\varepsilon = 1 - \frac{I^{S}_{Pb\text{-}212} - I^{B}_{Pb\text{-}212}}{I^{S}_{Ra\text{-}224} - I^{B}_{Ra\text{-}224}} \cdot \frac{p_{\gamma,\,Ra\text{-}224}}{p_{\gamma,\,Pa\text{-}212}} \quad (5)$$

where ε is the emanation coefficient, $I^{S}_{Pb\text{-}212}$ is the intensity of 239 keV gamma line of ^{212}Pb in the sample, $I^{B}_{Pb\text{-}212}$ is the background intensity measured without sample on 239 keV energy, $I^{S}_{Ra\text{-}224}$ is the intensity of 241 keV gamma line of ^{224}Ra in the sample, $I^{B}_{Ra\text{-}224}$ is the background intensity measured without sample on 241 keV energy, $p_{\gamma,\,Ra\text{-}224}$ is the probability of gamma emission of ^{224}Ra on 241 keV energy, $p_{\gamma,\,Pb\text{-}212}$ is the probability of gamma emission of ^{212}Pb on 239 keV energy.

Thoron activity concentration in kBq m^{-3} is calculated from emanation coefficient according to Equation 6[20]:

$$c = \frac{A_{Th\text{-}228} \cdot \varepsilon}{V} \quad (6)$$

where c is the thoron activity concentration (kBq m^{-3}), $A_{^{228}Th}$ is the ^{228}Th activity of the source (kBq), ε is the emanation coefficient, V is the reference volume (m^3).

The applied measuring arrangement is similar to accumulation thoron measurements; therefore, the accumulation method can also be used for determining emanation[21]. Ideally, emanation coefficients determined by different methods shall be equal. The accumulation method is suitable for determining emanation when free-exhalation occurs. This means the amounts of gas emanated and exhaled are equal. For thoron, due to the short half-life, the saturation sets within a few minutes (accumulation period). The activity concentration in saturation is proportional with the emanation coefficient.

Prior to the measurements, 15 g of the ceramic source sample was placed into a plastic cylinder equipped with valves and the thoron/radon trapped in the pores were removed by vacuum. Then the sample was placed into the accumulation chamber. (Sample contains ceramic spheres with a diameter of 2 mm, thus free-exhalation occurs.) The accumulation chamber is equipped with a fan to homogenize the thoron concentration. Thoron concentration in the accumulation chamber was monitored by the Sarad EQF 3220. The valves of the chamber were connected to the inlet and the outlet of the instrument. A filter was placed into the inlet tube to remove solid daughters. The accumulation space was 1400 cm^3. Thoron activity concentration was shown on the display of the instrument in kBq m^{-3}. The emanation coefficient is calculated from Equation 7:

$$\varepsilon_{Tn} = \frac{C_{Tn} V_A m_C}{m_{Th} S_{Th} m_F} \quad (7)$$

where ε_{Tn} is the emanation coefficient, C_{Tn} is the measured thoron activity concentration (kBq m^{-3}), V_A is the accumulation space volume (0.0014 m^3), m_C is the mass of the ceramic used for source preparation (g), m_{Th} is the mass of the thorium-nitrate added to the ceramic at source preparation (g), S_{Th} is the specific activity of natural thorium-nitrate (3.93 kBq g^{-1}), m_F is the mass of the fired ceramic (g).

3. Results and discussion

3.1. Scintillation techniques

In the first measurement, Sarad EQF 3220, Sarad RTM 2100, Pylon AB-5 and NDI instruments were applied, since the Durridge RAD7 was not available at that time. The Sarad EQF 3220 device registered the counts in every hour. The Sarad RTM 2100 device was measuring only for the first 30 hours period (due to inappropriate cable connections the power supply of instrument was not ensured), but the results are suitable for comparison. The thoron activity concentration values measured by the different instruments are presented on Figure 1. The uncertainties of the measurements have been given by the instruments.

Based on these, good agreement was found between the Pylon AB-5, Sarad EQF 3220 and Sarad RTM 2100 instruments. Values measured by the NDI system are a bit lower. A probable reason for this is that the efficiencies of the applied Lucas cells may not have been determined accurately for thoron measurements. An efficiency calibration is necessary for its determination in the future. Beside this , three outstanding values were found in case of integral measurement with NDI system. These measurements were performed with the same scintillation cell; therefore, the supposed reason of the differences is the failure of the cell. At the calculation of average concentration these values had not been considered.

The comparison of Durridge RAD7 device with the Pylon AB-5, as the supposed reference instrument, was carried out at a later date. The measurement was performed as previously described. Thoron activity concentrations measured by RAD7 and AB-5 are presented on Figure 2. Based on these, the deviation of RAD7 results is higher than those of the Sarad instruments, probably owing to the RAD7's shorter measuring periods. The measuring cycle of RAD7 is 5 minutes; however, SARAD instruments are measuring one hour periods. Lower measurement time causes higher

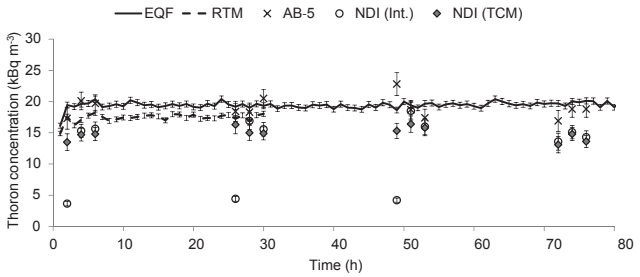

Fig. 1. Thoron concentrations measured by different instructments.

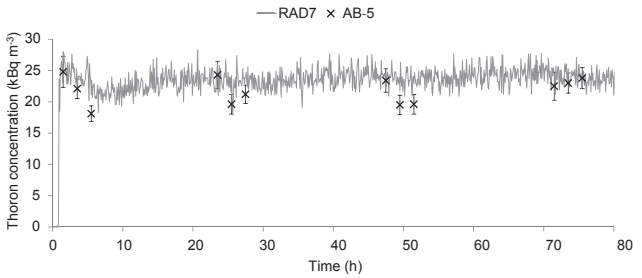

Fig. 2. Comparison of the measurement result of Durridge RAD7 and Pylon AB-5 instruments.

uncertainty due to the stochastic nature of radioactive decay. However, the results of the two methods show a good correlation; the difference between the averages is less than 5 %.

Based on the results, the Pylon AB-5 device with TCM method is a suitable reference instrument, since good correlations were found with all tested active devices (the differences were less than 10 % in all cases).

3.2. Gamma spectrometry

The emanation coefficient was determined in two different ways: based on the gamma spectra and by accumulation method. The technique is suitable if the emanation coefficients determined by the two ways are equal. The emanation coefficient calculated from gamma spectra is 0.38; while by accumulation method it is 0.13.

The problem of this method is that free-exhalation doesn't occur in this case, since the ceramic spheres are in a sealed plastic cylinder. Accordingly only a "stripping factor" can be determined instead of emanation coefficient. The stripping factor has been defined as that ratio of the total generated thoron amount which can be transferred to the reference volume from the cylinder.

For the determination of stripping factor it is necessary to determine the ^{212}Pb and ^{224}Ra activity content of the source in secular equilibrium. For this experiment, a high activity thoron source was used. The resolution of the detector was not high enough to separate the close energy peaks of ^{212}Pb and ^{224}Ra, therefore the total intensity of ^{212}Pb and ^{224}Ra was determined. After that, the thoron gas was stripping out continuously from the source for a few days while the ^{212}Pb excess decayed. Then the total intensity of ^{212}Pb and ^{224}Ra was determined again. The stripping factor is defined as follows (Equation 8):

$$\sigma = \frac{I_E}{I_S} \tag{8}$$

where I_E is the total intensity measured at approx. 240 keV energy in secular equilibrium, I_S is the total intensity measured at approx. 240 keV energy after stripping the thoron gas out.

In this case, a 0.046 stripping factor has been calculated from which approx. 25 kBq m^{-3} thoron activity concentration has been estimated inside the calibration chamber. (Based on formal gamma spectrometric measurements the ^{232}Th activity of the source is 110.67 kBq, the volume of the calibration chamber is 0.2 m^3.) This is in accordance with the experience that 20-25 kBq m^{-3} thoron activity concentration can be set in the calibration chamber with this source.

Based on the experiments, this method can be used only for preliminary, informative measurements, since the structure of the ceramic source does not compile with the requirements of free-exhalation . However, for this purpose other, simpler techniques (e.g. accumulation method) can be used effectively as well. Based on the principle of the method, it could be able to estimate the producible thoron concentration with a given ceramic source. However, this could provide only informative data due to the insufficiently high resolution of the detector; it could not be used as reference technique. Moreover, the application of HPGe detector during continuous calibration measurements is complicated due to its design. However, for the application of this method, high energy resolution capability is necessary which cannot be provided by other detector types with simpler design (e.g. NaI(Tl) scintillator).

Based on the results, scintillation counting with Pylon AB-5 and calculation according to TCM method is proposed as reference method for thoron measurements.

4. Conclusions

During this study, various scintillation and gamma spectrometric techniques were tested for thoron measurements during calibration of CR-39 based SSNTDs. Based on the results, it can be concluded that reference measurements by gamma spectrometry are insufficient in case of calibration measurements with ceramic thoron sources. For this purpose, grab sampling with Lucas cells with ZnS(Ag) scintillator coating and counting according to TCM method are proposed. In case of RRI chamber, Pylon AB-5 monitor with 300A Lucas cell

has been applied.

Conflict of Interest Disclosure

The authors declare that they have no conflict of interest.

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