

## APPLICATION OF LIQUID SCINTILLATION SPECTROMETRY FOR RADON AND RADON PROGENY MEASUREMENTS IN AIR

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**ABSTRACT.** Liquid scintillation counting (LSC) is commonly applied in environmental monitoring of different radionuclides. One possible application of LSC is measurement of radon progeny. There are certain advantages of this method, especially the high counting efficiency for alpha and beta particles emitted by  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ , and  $^{214}\text{Po}$ . This advantage was pointed out several years ago when such methods were applied for calibrating portable monitors for Rn progeny, especially due to the fact that for Rn progeny, no standard atmosphere exists. On the other hand, alpha and beta particles can be counted in a liquid scintillator with an efficiency close to 100%. Rn progeny can be collected on a filter, which after immersion in the liquid scintillator becomes transparent and can be counted without significant quenching. Therefore, such a method can be regarded as absolute and thus be used widely for monitoring Rn progeny. The main drawback in the past was the lack of portable LS counters; however, recently, portable counters have become available. Furthermore, Rn concentration in air can be measured by using charcoal canisters to collect Rn and further extracting the Rn into a liquid scintillator. A very quick measurement (5-min grab sampling) for outdoor Rn is possible when the charcoal layer is very thin. A combination of both methods enables quick and reliable measurements of Rn and Rn progeny concentration in outdoor and indoor air.

### INTRODUCTION

The risk of radiation caused by radon was first recognized in uranium mines; therefore, methods for measuring Rn progeny concentration and instrumentation were developed for the uranium industry (Tsivoglou 1953; Kusnetz 1956). Later, enhanced concentrations of Rn and its progenies were measured in other types of underground mines (Sciocchetti 1981; Lebecka 1983). In Poland, a research program for investigations of Rn and progenies in coal mines was started by the Laboratory of Radiometry in the Central Mining Institute in the early 1980s (Lebecka 1985).

Investigations of Rn and progenies in indoor and outdoor air using different methods and instruments (NCRP 1988) are very widespread. Problems that may appear during such measurements are related to the detection limit, accuracy, and precision of the applied techniques. Thus, our efforts focused on the liquid scintillation technique, in which measurement of alpha and beta particles with an efficiency close to 100% is possible. The biggest problem to solve was a possible quenching caused by the filter in the scintillator. A membrane filter was applied and became transparent in a toluene-based liquid scintillator (Chałupnik and Lebecka 1986). This method was first applied as a calibration method only because at that time there were no portable LS counters.

Rn concentration in air can be measured using a charcoal canister. Charcoal canisters are used to collect Rn from the air, and exposure is followed by an extraction of Rn from the charcoal into a liquid scintillator. A quick sampling of Rn from the air is possible when the charcoal layer is very thin, but humidity in the air negatively influences the results. Therefore, sampling time must be <10 min. After exposure, charcoal pellets are transferred into containers and sealed tightly. Subsequent extraction and measurement can be done in the laboratory due to the long half-life of Rn.

Rn progeny can be collected on a filter simultaneously during the same measurement period. In this case, measurement must be done immediately after sampling. The filter, immersed in the liquid scintillator, becomes transparent and can be counted using a counting regime like the Thomas method (Thomas 1970). The main drawback of the method was that for a long time there was a lack of portable LS counters; fortunately, in the last several years such counters have become available. This method is absolute and can be used for Rn progeny monitoring (Chałupnik and Kies 2003).

A combination of both methods allows for the opportunity to simultaneously make grab-sample measurements of Rn and progeny concentration in air. In both cases, detection limits are very low due to the high counting efficiency of alpha and beta particles in the liquid scintillators.

### Radon Progeny Measurements

The counting regime of the method is the classic Thomas method (Thomas 1970), which was chosen because it can give not only potential alpha energy concentration (PAEC) but also concentrations of any single isotope,  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$  (the same as the concentration of  $^{214}\text{Po}$ ).

The disintegration of isotopes from the same series, e.g. Rn progeny, is described by Bateman (1910):

$$\frac{dN_i}{dt} = \lambda_{i-1} \times N_{i-1} - \lambda_i \times N_i \quad (1)$$

where  $N_i$  is the number of atoms of  $i$ -th isotope from the series, and  $\lambda_i$  is the decay constant ( $\text{s}^{-1}$ ).

For describing the changes of activity when collecting isotopes on the filter during sampling, an additional part must be added. If the flow rate through the filter is  $V$  (L/min) and the concentration of atoms of the  $i$ -th isotope in air is  $n_i$ , then we have

$$\frac{dN_i}{dt} = \lambda_{i-1} \times N_{i-1} - \lambda_i \times N_i + V \times n_i \quad (2)$$

Typical solutions are cited in previous literature (e.g. NCRP 1988; Thomas 1970) but only for alpha decays. As in liquid scintillators, alpha and beta particles can be counted simultaneously; therefore, the solution has to be recalculated (Chałupnik et al. 1985).

The solution for the Thomas method (sampling time  $tp = 10$  min, and 3 subsequent counting periods, between 2–5, 6–20, and 21–30 min after the sampling period) is as follows (Chałupnik 1996):

$$\begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} = \begin{bmatrix} 523.0 & 2256.4 & 2684.4 \\ 1470.0 & 11279.0 & 9054.8 \\ 520.0 & 7012.8 & 3723.4 \end{bmatrix} \times \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} \times V \quad (3)$$

where  $N_1$ ,  $N_2$ , and  $N_3$  are the number of counts obtained during the first, second, and third counting period, respectively; and  $V$  is the flowrate through the filter (L/min).

Since we would like to calculate concentrations of  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$ , a reverse matrix must be found for the matrix of coefficients (Equation 3), which gives us:

$$\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} 52.690 & -25.570 & 24.175 \\ -4.775 & 0.580 & 2.030 \\ -2.605 & 4.530 & -6.450 \end{bmatrix} \times \begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} \times \frac{10^{-4}}{V} \quad (4)$$

It is then possible to calculate the potential alpha energy concentration,  $C\alpha$  (Evans 1969):

$$C\alpha = 0.579 \times C_A + 2.850 \times C_B + 2.087 \times C_C \quad (5)$$

where  $C\alpha$  is  $\mu\text{J}/\text{m}^3$ ; and  $C_A$ ,  $C_B$ , and  $C_C$  are  $\text{kBq}/\text{m}^3$ .

Finally,  $C\alpha$  can be expressed as a function of  $N_1$ ,  $N_2$ , and  $N_3$ :

$$C\alpha = \frac{(11.430 \times N_1 - 3.650 \times N_2 + 6.250 \times N_3) \times 10^{-4}}{V} \quad (6)$$

Using these formulas based on the measurement results of the filter in the LS counter, one can calculate the concentrations of particular isotopes and potential alpha energy concentration.

### **USING THE TRIATHLER LS COUNTER FOR RADON PROGENY MONITORING IN AIR**

Recently, portable LS spectrometers appeared, enabling the monitoring of Rn progeny in different environments. One of the portable monitors is the Triathler (Hidex Company, Finland).

One important issue is the application of a pump with high flow rate, because the detection limit is dependent on the total amount of air pumped through the filter during sampling (see Equations 4 and 6). The pump applied in our experiments was completely clogged when membrane filters were tested. Therefore, fiberglass filters (Muster and Nagel) were used. Using fiberglass filters ensured the transparency of the filters being submerged in the scintillator (counting efficiency close to 100%) and a enabled high flow rate of  $\sim 300$  L/min.

The next step was to choose a proper scintillation cocktail. A toluene-based scintillator is usually used for such purposes, but we used the cocktail OptiScint HiSafe 3 (PerkinElmer, USA; based on DIN), which provides the same performance as a toluene-based one. Typical glass vials with 12 mL of the cocktail were used during measurements.

Measurements were made of the background in the wide window in Triathler. The clean filter was submerged into the scintillator and the blank sample was measured. In the wide counting window, we found a rather high instrument background ranging from 150 to 250 cpm. This is the main reason that a high-volume pump must be used for the air sampling.

Next, we calculated of the lower limit of detection (LLD) according to Currie (1968). The following assumptions were made: flow rate 250 L/min, pumping time 10 min, and background  $\sim 200$  cpm. The detection limit for alpha potential energy is  $\text{LLD} \approx 0.0008 \mu\text{J}/\text{m}^3$ . Despite the relatively high background, the detection limit is very low due to the very good counting efficiency ( $\sim 100\%$ ) and high flow rate, which compensate for the background influence.

### **RESULTS OF FIELD EXPERIMENTS**

Our measurements were performed in buildings in the Physics Department of Luxembourg University (CU) in laboratories, cellars, and outdoors. Some additional experiments were done in an abandoned gypsum mine (Chałupnik and Kies 2003).

Measurements from laboratories in CU showed very low concentrations of potential alpha energy of Rn progeny ( $0.005\text{--}0.013 \mu\text{J}/\text{m}^3$ ). This value corresponds to the value for outdoor air, but measurements were done during a hot summer, with open windows in laboratories, which may explain our results. This hypothesis can be supported by the strong disequilibrium among particular Rn progeny isotopes, most likely due to the high ventilation rate. Other measurements were done in the cellars and underground car park of the Physics Department building. Concentrations of total alpha energy ranged from  $0.5\text{--}1.2 \mu\text{J}/\text{m}^3$ , while concentrations of  $^{218}\text{Po}$  ranged from  $300\text{--}700 \text{Bq}/\text{m}^3$ . A Rn cham-

ber at CU is located in one of these cellars. Results from confined rooms, with limited ventilation and exhalation of Rn from the ground underneath the building, were in agreement with our expectations.

Our next step was an attempt to measure Rn progeny concentrations outside the building. We found that such measurements must be performed very carefully, and that it is especially important to avoid exposing the scintillator vial to sunlight. Luminescence, induced in the scintillator, significantly increases the background, and the results of the first measurement were inaccurate. The solution is to keep the vial with the scintillator in a place with no direct sunlight. Other measurements done simultaneously and in the following days showed that such monitoring can be done with very good precision and accuracy.

The final step was the monitoring of Rn progeny concentrations in an abandoned gypsum mine. Initially, we applied a high-volume pump for air sampling, but results were poor. Exceedingly high concentrations of Rn progeny collected on the filter subsequently produced an exceedingly high count rate in the LS counter. Therefore, we decided to use a pump with much lower flow rate (7 L/min). Filters from personal dust masks were also measured. We note the very good agreement of results obtained for filters from the personal respirator. This respirator was used for inhalation (10 min), and the filter was then transferred into the liquid scintillator and counted. When we assumed the flow rate through the mask at 20 L/min, the results were close to those using the mechanic pump.

We found that the concentrations of potential alpha energy in the mine were  $20 \mu\text{J}/\text{m}^3$ . Unfortunately, we were not able to compare our results with any other instrument for Rn progeny monitoring. At the same time, Rn monitoring in the mine was done by using an AlfaGuard system, giving results of 10–12 kBq/m<sup>3</sup>, which were in good agreement with calculated concentrations of <sup>218</sup>Po.

#### **APPLICATION OF ACTIVATED CHARCOAL CANISTERS AND LSC FOR RADON MONITORING**

The use of the activated charcoal canisters for Rn monitoring in air is a well-known method, and its applications are widespread. Gamma spectrometry is often used for measuring canisters after exposure, but LSC is also used for this purpose. A commercial application for charcoal detectors and LSC (PicoRad, Niton) is well known. Charcoal canisters are typically used for screening Rn concentration in dwellings (Wysocka et al. 1996, 1998), but charcoal canisters are used also for Rn exhalation measurements (Cosma et al. 1999; Chalupnik and Wysocka 2003).

We developed our own charcoal canisters for Rn screening in houses (Wysocka et al. 1998). The detector is a scintillation glass vial with 5 g of activated charcoal. At the top of the vial, a cotton filter is placed. After exposure, the vial with charcoal is attached via a special connector with another vial containing 18 mL of toluene-based scintillator. This special connector allows the transfer of the liquid scintillator to the vial with charcoal. The extraction takes place within 10 min, after which the extraction scintillator is transferred back to its vial. A special sieve prevents the transfer of charcoal pellets in the scintillator.

Calibration of the charcoal canisters was done several times in a Rn chamber. The calibration curves for 2 types of activated charcoal are presented in Figure 1. The upper line shows the Rn concentration in the chamber, while the 2 lower curves show the differences between readouts of charcoal detectors with 2 types of activated charcoal. This figure reveals that the exposure time of such detectors should be at least 48 hr. Another very important factor is the influence of air humidity. There-

fore, canisters should be weighed before and after exposure to enable correction for the humidity effect.

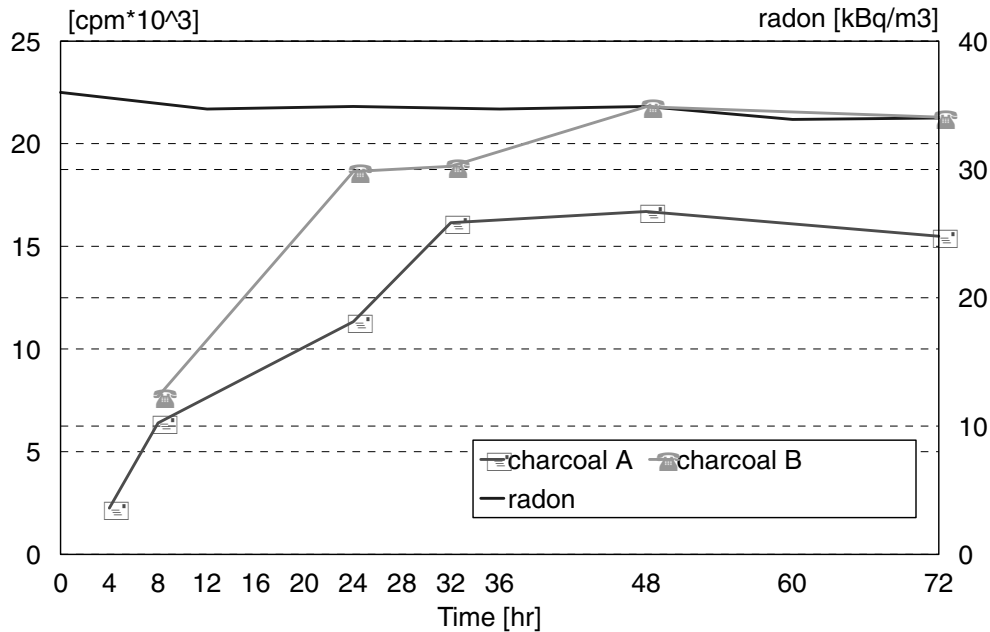


Figure 1 Calibration curves of charcoal detectors

These charcoal detectors have been used for several years for quick screening of Rn concentration in dwellings in the Upper Silesia region (Wysocka et al. 1998). Results of the screening measurements were in good agreement with the results of monitoring done with nuclear track detectors.

Another application of charcoal canisters is the assessment of Rn exhalation from the ground. A charcoal detector is placed inside the accumulation chamber for several hours to collect Rn exhaling from the ground surface. Use of the method showed significant differences with the results obtained using Lucas cells. Analysis of the possible reasons for the discrepancy led to the conclusion that the calibration procedure was improper. Preliminary calibration was done in the Rn chamber with the stable Rn concentration, but during exhalation, Rn concentration in the accumulation chamber rose; thus, adsorption of Rn on charcoal is different. Another calibration procedure must be applied (Chałupnik and Wysocka 2003) when Rn concentration increases from the background level. Results of the calibration are shown in Figure 2. After applying a new calibration factor, results of simultaneous measurements using Lucas cells and charcoal canisters became consistent.

While testing the open-face charcoal detectors in the Rn chamber, we found that the canisters displayed a very high sensitivity to relative humidity but also a very fast response of the detector to Rn concentration in air. Although the sensitivity to air humidity limited the use of open-face detectors for measurement in dwellings, the fast response for Rn concentration was very promising for developing a fast Rn monitoring method.

We used 5 g of activated charcoal as a single-layer, open-face detector for quickly monitoring Rn concentration in air. The technique of exposure and measurement is as follows. A single layer of

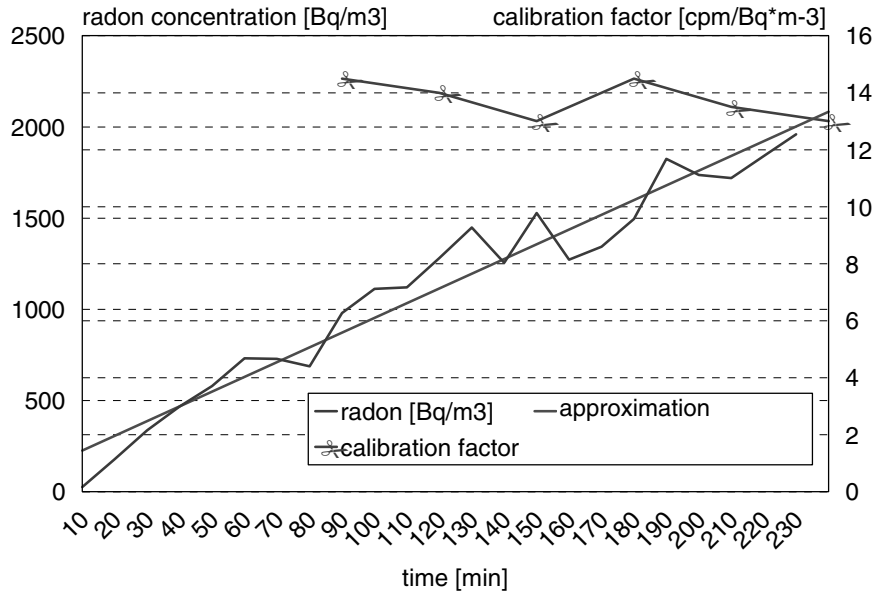


Figure 2 Calibration of charcoal canisters for Rn exhalation measurements

activated charcoal is exposed on the flat support; after exposure, it must be quickly transferred into a scintillation vial via a funnel; finally, this vial should be capped and taken to the laboratory, where Rn is extracted from charcoal into a liquid scintillator and the resulting sample is measured in the LS counter. Calibration in the Rn chamber, where the relative humidity was ~80% and the temperature 20 °C, was done with exposure times starting at 1 hr. Results of this calibration (of open-face detectors and typical detectors, in scintillation vials) are shown in Figure 3.

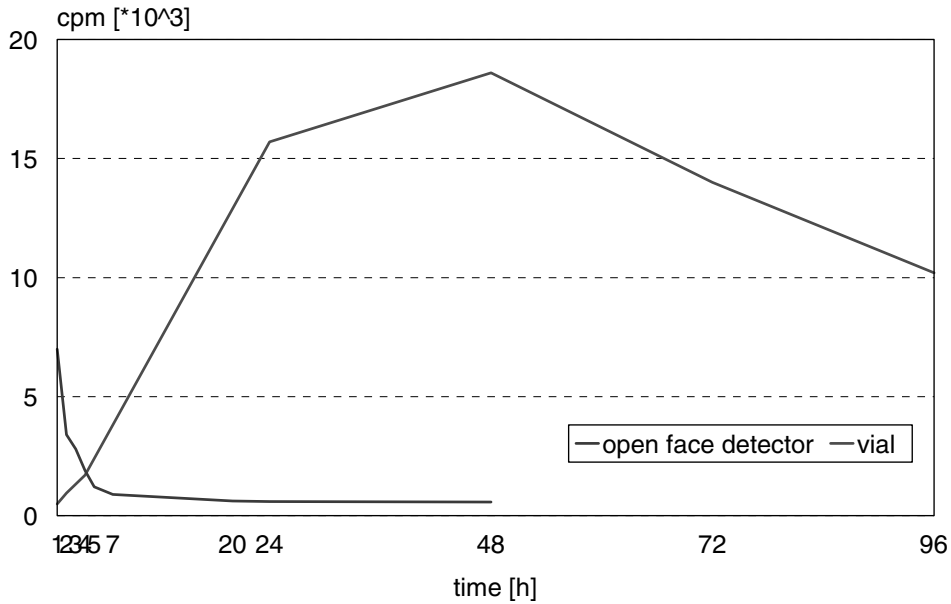


Figure 3 Readouts from the open-face charcoal detector (lower line) and the normal detector (upper line)

Results of the preliminary calibration showed that exposure longer than 1 hr is too long for the open-face detector. We did not find a maximum value in the readouts of these detectors, only the decrease of count-rate, measured in LSC. This decrease is faster than the decrease due to the decay of Rn; therefore, the only possible explanation is the competing effect of humidity.

Finally, we decided to make very short exposures, of which the shortest possible time was 3 min. Results of these short exposures in the Rn chamber are shown in Figure 4. Due to our calibration, the maximum of the readouts is reached for exposures between 5–8 min, and soon after, the influence of humidity becomes significant. When the exposure time is 30 min, the detector sensitivity decreases by a factor of 2, and after 1 hr of exposure by a factor of 3. On the other hand, the maximum sensitivity between 5–8 min of exposure allows for simultaneous grab measurements of Rn and progeny in air.

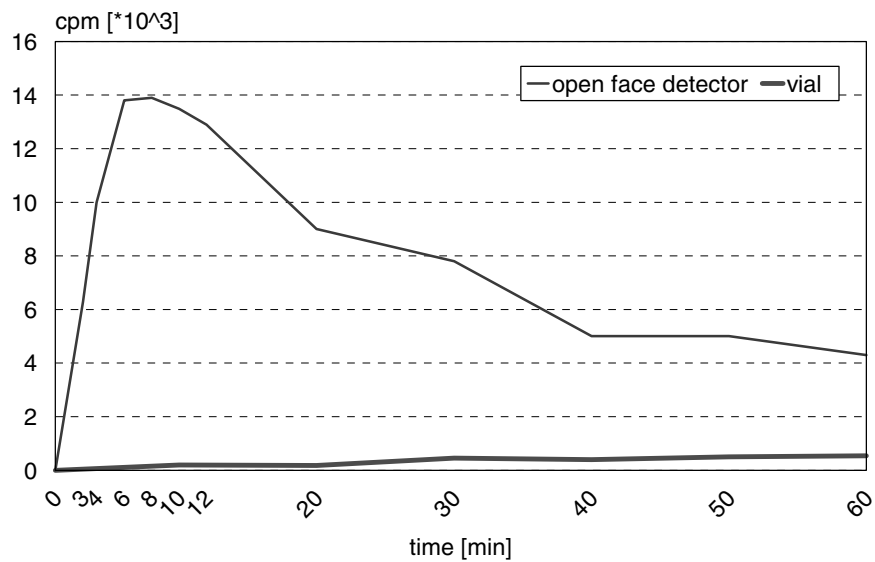


Figure 4 Calibration of open-face detectors in Rn chamber with a short exposure time; the upper line shows the response of open-face detectors, while the lower line represents the readouts of canisters.

For monitoring Rn concentration in air with open-face charcoal detectors, it is not necessary to use a portable LS spectrometer. After exposure of detectors and transfer of charcoal into the scintillation vial, detectors can be taken to the laboratory, and after extraction of Rn into the liquid scintillator, samples can be measured in a normal LS spectrometer. The detection limit for Rn concentration in air depends on the background of the LS counter; therefore, low-level LSS is required for outdoor measurements.

When Quantulus™ is used for measuring Rn samples, the lower limit of detection (count time 30 min, 5 g of charcoal) is ~0.5 Bq/m<sup>3</sup>.

**SIMULTANEOUS MEASUREMENT OF RADON AND PROGENY BY LSC**

As mentioned previously, it is possible to measure Rn concentration using charcoal canisters and LSC, and also possible to measure Rn progeny concentration by air filtration and filter measurement via LSC. The problem was how to do both measurements simultaneously.

One of the approaches to this problem was to apply charcoal in the scintillation vials for Rn monitoring (but the exposure time was at least 6 hr) and simultaneous grab sampling of Rn progeny and measuring in a portable LS spectrometer, Triathler (Chatupnik and Kies 2003). This technique can be used for measurement in dwellings or other places with relatively stable Rn concentration. However, for outdoor air measurements the response time of charcoal canisters in vials is too slow. A new technique of charcoal exposure is therefore proposed using a single-layer, open-face charcoal detector. Despite the fact that such a detector is very sensitive to air humidity, the response time is very quick, only 5–8 min, which enables simultaneous sampling of air for Rn and Rn progeny monitoring.

The method for simultaneously measuring Rn and progeny in air by means of LSC can be described as follows:

- The method requires 2 LS spectrometers: a low-level counter for Rn measurements and a portable LS spectrometer for Rn progeny monitoring.
- For sampling Rn progeny in air, a pump with a high flow rate is necessary (at least 100 L/min) as are filters that become transparent in a toluene-based liquid scintillator (membrane or fiber-glass filters).
- Sampling of Rn progeny is done for 10 min, and then the filter with collected aerosols is merged into the vial with liquid scintillator and measured according to the Thomas (1970) method in the portable LS spectrometer Triathler.
- For Rn monitoring, a charcoal detector is required, which is exposed during the same period as air sampling for Rn progeny as a single-layer, open-face bed.
- The exposure time should be 5–8 min, and after exposure the charcoal must be quickly transferred into the vial and sealed immediately.
- Extraction of Rn from charcoal and measurement of the obtained sample can be done in the laboratory. Measurement should be done with a low-level LS spectrometer to ensure a low detection limit for Rn. If the LS spectrometer is equipped with the alpha/beta separation feature, the LLD level for Rn concentration will be lower.

## CONCLUSION

We tested the possibility of using a portable LS counter (Triathler, Hidex Oy, Finland) for measuring Rn progeny concentration in air. Tests were performed at Centre Universitaire (Luxembourg) and results of preliminary measurements were satisfactory.

The application of a high-volume pump enables use of the method for outdoor measurements. The sampling time must be short enough (usually 10 min) to allow for an accurate calculation of potential alpha energy concentration, followed by the transfer of the filter into liquid scintillator, and measurement accordingly to the Thomas method. Thus, the detection limit can be very low: potential alpha energy concentration is  $\approx 0.001$  J/m<sup>3</sup>. We note that the method can be stated as absolute, and problems involving calibration can be avoided.

Using charcoal detectors enables measurement of low concentration of Rn in air when single-layer, open-face detectors are used. The exposure time of such detectors should not exceed 10 min. The extraction and measurement can be done in laboratory conditions. When a low-level LS spectrometer like Quantulus is used, the lower limit of detection for this method can reach 0.5 Bq/m<sup>3</sup>.

Sampling of air for Rn and Rn progeny can be done simultaneously and detection limits for both methods are sufficient to allow measurements even in outdoor air with very good precision and accuracy.

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