Preparation of multi-purpose radon emanation sources

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Abstract

The aim of this work was to prepare reference radon emanation sources traceable to primary standards to be used for radon-in-air as well as radon-in-water experiments. The feasibility of making stable radon emanation sources by drop deposition and chemisorption was studied. Experimental emanation coefficients for sources made by drop deposition and chemisorption ranged from 0.10 to 0.74 and from 0.18 to 0.25, respectively. These relatively low emanation coefficient values suggest that further method developments would be desirable. Proposals are made to improve chemisorption yield during source preparation and to obtain more accurate measurements on radon emanation coefficient.

Keywords Radon emanation · Chemisorption · Drop deposition · Radon-in-water · MetroRadon

Article highlights

- The aim was to make reference radon emanation sources.
- Drop deposition and chemisorption radon emanation sources were tested.
- Authors propose changes to increase chemisorption yield and emanation coefficient.

Introduction

Despite decades of history of radon-in-air measurements [1], accurate and SI traceable radon activity concentration measurements in air are still part of scientific research and discussions [2, 3]. It was further stimulated by the European Council's new Basic Safety Standard (BSS) [4] that for the first time also deals with low radon activity concentrations ($< 300 \text{ Bq/m}^3$).

Therefore, there was a big demand from the organisations dealing with radon measurements for reliable, metrological sound calibration methods and sources at low radon concentrations ($< 300 \text{ Bq/m}^3$) to fulfil the BSS requirements.

This knowledge gap initiated the Metrology for Radon Monitoring (MetroRADON) European Metrology Programme for Innovation and Research (EMPIR) project [3]. Within this project an important objective was to develop radon emanation sources and procedures for the traceable calibration of radon measurement instruments below 300 Bq/m^3 with relative uncertainty of $\leq 5\%$ (at $k = 1$) [1, 3]. JRC contributed to the development of novel ^{222}Rn (radon) and ^{220}Rn (thoron) radioactive reference sources traceable to primary standards with stable and known radon emanation, one of the main goals in the MetroRadon project [3]. The two main emanation source preparation methods, considered at the beginning of the project, were electrodeposition and co-precipitation. Since PTB (Physikalisch-Technische Bundesanstalt, Germany) chose to develop electrodeposited sources [5] and LNH (Laboratoire National Henri Becquerel, France) focused in barium stearate co-precipitated source preparation [3], JRC studied drop deposition and chemisorption preparations of radon sources to avoid duplication of the work by other project partner.

Along with the MetroRadon project objectives, JRC had to take the priorities within its own work program into account, which includes radon-in-water measurement [6–8]. On that basis, we set three main goals for the radon emanation source preparation at JRC-Geel. The first goal was to prepare multi-purpose calibration or reference radon sources suitable for radon-in-air and radon-in-water experiments. The second goal focused on the environmental impact and waste production; we wanted to reduce the energy and chemical consumption and

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eventually waste. The third requirement, linked to the previous one, was to reuse the solution for source preparation several times by feeding the necessary initial ^{226}Ra activity from a certified reference solution.

The concept of using materials emanating radon is not very new. Many different materials were used to make radon-rich water or atmospheres in the past mainly for medical and rejuvenating purposes [9]. The radium rich material was either immersed in water or put in a closed jar until the desired radon activity concentration was reached. The same principle as these historical approaches can be used with materials where the emanation coefficient and initial ^{226}Ra activity are more accurately known and even metrological traceability can be established [10, 11].

Probably the first metrological traceable radon-in-water standard generator was developed by the National Institute of Standards and Technology in USA (formerly called as National Bureau of Standards) in the 1980's [10]. It was based on polyethylene-encapsulated standardised ^{226}Ra solution and used to calibrate radon in water measurement systems. Later this type of polyethylene- encapsulated sources was also used as radon emanation standards for radon-in-air measurements.

Radon generators can be produced from crystalline, amorphous and porous materials but their emanation power can vary in wide range. In general crystalline materials show lower emanation power-few percent-while the emanation power of porous materials can reach close to 100% in certain cases [12].

During chemisorption, radium selective discs can be used, as developed by Surbeck [13, 14] for analysing environmental water samples [15–18]. The development of these discs was intended for alpha-particle spectrometry source preparation saving a significant amount of reagents and analyst's time. The surfaces of the discs are covered with a thin layer of radium selective material (manganese-dioxide) where radium is adsorbed very close to the surface and strongly on the disc. The adsorbed ^{226}Ra is determined by alpha-particle spectrometry activity measurements and the emanation coefficient by a radon emanation setup. The emanation coefficient is determined as the ^{222}Rn fraction, generated during the decay of ^{226}Ra in a matrix that escapes the host material and released into the surrounding air.

This paper intends to give a brief description on the radon emanation source preparation at JRC and the first applications of these new emanation sources.

Experimental

The certified radioactive ^{226}Ra solution containing Ba-carrier was provided by the Czech Metrological Institute (CMI) with traceable massic activity of 3.526 (18) kBq/g ($k = 1$).

For the drop deposition method, a known activity of ^{226}Ra was deposited on paper filter. It dried under ambient conditions and afterwards was sealed in a commercially available low density polyethylene (LDPE) foil. The average LDPE foil thickness was measured by an optical focusing device at $(46 \pm 4) \mu\text{m}$, which is sufficiently thin for being permeable for radon. All used reagents were of analytical grade. Deionized laboratory water was used for the dilutions.

For the chemisorption method, manganese dioxide based discs were purchased from TrisKem International (TrisKem). The discs were exposed for 6 h to a solution of 100 mL of water containing the dispensed ^{226}Ra -standard solution and stirred with approximately 200 rpm. The radium specific discs were placed in a polyethylene holder and immersed in the liquid containing dispensed 200–700 Bq ^{226}Ra standard solution. According to literature > 90% of the radium activity present in the sample can be adsorbed after 6 h of exposure [16]. The emanated radon was measured by a RAD 7 (DurrIDGE Inc.) and an Alphaguard (Saphymo) active radon monitors. The schematic overview of the experimental design is presented in Fig. 1.

Results and discussion

One of the pitfalls of the drop deposition method is that radon permeability strongly depends on environmental parameters like temperature, humidity and pressure [19]. Therefore, it was proposed by the project partners to quantify the relation of the radon permeability to the environmental conditions. JRC did not have a radon chamber with controlled atmosphere during this work. Therefore, the relation between radon emanation and environmental parameters was not quantified in our study. It was noted that temperature and pressure sometimes changed during the experiments which might result in unstable emanation. The following environmental parameters were recorded during an emanation experiment: $t = 19.9\text{--}24.5\text{ }^\circ\text{C}$, $p = 975\text{--}1035\text{ mbar}$ and 24–40% of relative humidity. To overcome the

Fig. 1 Schematic overview of the emanation experimental design

environmental dependence on the emanation through foils, chemisorption sources were prepared using radium specific discs.

The emanation coefficients of the JRC radon emanation sources by the two methods are compared to radon emanation sources from the literature based on different preparation approaches in Table 1.

One of the deposition sources, (RnDep3), was sealed in a 200 μm thick plastic film using a laminating machine. This laminating foil was proved too thick resulting in a significant drop (from 74 to 10 %) in emanation power.

Another shortcoming of our sources is the slow kinetics of radon emanation. It was observed that 2–3 days are needed to reach the saturation point in our small volume (2 L) setup from an 588 Bq ^{226}Ra activity source with a maximum activity concentration of 44.3 (26) kBq/m^3 measured by AlphaGuard.

The emanation sources were already tested in radon-in-water measurements where elevated radon activity concentration had to be produced in a low volume (0.2–1 L) container [6]. The emanation sources were placed in an LDPE foil and immersed in a 1-L heat shock resistant borosilicate glass bottle with a gas-tight but flexible screw cap designed for volatile organic material storage. A more detailed description on the bottle and radon-in water setup is presented elsewhere [6, 7]. After 5 days of exposure approximately 275 Bq/kg ^{222}Rn massic activity was measured. The maximum (equilibrium) of 525 Bq/kg ^{222}Rn was reached after 25 days of exposure.

The homogeneity of the adsorbed radium over the disc surface of two chemisorption sources was tested by autoradiography as seen in Fig. 2.

Concentric circular region-of-interests are defined with the centre corresponding to the the physical centre of the source, the zero distance point (“0”) in the graphs of Fig. 2. The radial activity distribution is presented as digital light unit density over a surface area (DLU mm^{-2}). It

Fig. 2 Autoradiography and activity distribution of radium on the MnO_2 chemisorption sources. Red colour represents areas with high activity, blue with low activity, white with zero activity

was recorded along a line through the centre of the sources in 85 μm /pixels steps and 30 minutes approximate exposure time. is taken at the centre of the source. The relative weights shown in the lower part of Fig. 2, are the DLU of a ring over the DLU of the net sum of all the area divided by the surface area of that ring over the surface area of the nearest inner ring. The ^{226}Ra activities of the sources were between 60 and 80 Bq.

As seen in Fig. 2, the deposited activity along the surface of the MnO_2 coated source (Metro-Rn02) can be considered homogeneous. This source preparation method is a very good candidate for preparing homogeneous emanation sources. On the downside, we still observe very low ^{226}Ra adsorption yield from the initial ^{226}Ra stock solution (< 10–30%) and low emanation power that suggests the need for further research.

Table 1 Summary of radon emanation sources from JRC and other studies with their emanation coefficients (dimensionless) and combined standard uncertainty

Source code or reference	Preparation mode	Material	Emanation coefficient	Relative uncertainty (u_{rel})
RnDdep1	Drop deposition	Paper filter	0.67 ± 0.05	7.4%
RnDep2	Drop deposition (filter)	Paper filter	0.74 ± 0.04	5.6%
RnDep3	Drop deposition (laminated filter)	Paper filter	0.10 ± 0.03	30%
Metro-Rn02	Chemisorption	MnO_2 disk	0.20 ± 0.03	15%
Metro-Rn04	Chemisorption	MnO_2 disk	0.18 ± 0.03	17%
Metro-Rn05	Chemisorption	MnO_2 disk	0.25 ± 0.04	16%
PTB [5]	Electrodeposition	Stainless steel disk	0.6–0.9	< 2%
BJ [20]	Coprecipitation–chemisorption	Complex silica gels	0.4–0.97	–
HL [21]	Coprecipitation–coevaporation	Ba-stearate	0.998 (thoron)	–

Table 2 Proposed modification of the emanation source preparation experimental parameters

Drop-deposition source	Chemisorption source
Changing the target materials: glass, metal (Ni steel) for better adhesion of drop deposited ^{226}Ra	Change lab-ware materials: glass, or polyethylene
Pre-treating the target disk with a seeding agent including colloidal silica to form more uniform crystals, thus more stable and uniform emanation	Increase the contact time between MnO_2 coated disk and the ^{226}Ra -bearing solution to increase the chemisorption yield
Thermal treatment of the target disk, including ^{226}Ra , to convert ^{226}Ra to oxide and fix it on the surface	Chemisorption of radium on chromatographic resins [22] or in clay based porous mineral matrix [23]

The environment related goals to reduce waste, energy consumption and chemicals can be achieved by applying the MnO_2 disk source preparation approach. The procedure needs limited resources: few basic lab wares, MnO_2 disk, stirrer, about 100 mL water and depending on the required activity maximum few mL of standardised ^{226}Ra solution.

^{226}Ra is fixed on the MnO_2 coated disk and stays there unless this upper layer is dissolved or physically removed. Therefore, the risk of contaminating the experimental setup is low comparing to cases when powder type radon emanation sources or radon emanation sources are not fixed to a carrier or the material used for encapsulation is damaged.

MnO_2 coated disks can be handled freely and placed directly into the experimental setup without extra precautions. The adsorbed ^{226}Ra activity could be directly determined accurately by placing the disk in a defined solid angle alpha-particle spectrometry setup.

On the other hand, there are still difficulties to determine the total ^{226}Ra activity with the desired accuracy (usually by gamma-ray spectrometry) and the emanation power correctly in powders or solid materials.

There is another drawback of inorganic porous gels based on heavy-alkali-earth metal hydroxides. Hydrated silicic acid and silica gel based emanation sources are sensitive to humidity [20]. They adsorb moisture from the air in their pores that affects the emanation power and can fluctuate in time.

One of the aims of the MetroRadon project was to develop radon and thoron reference sources with stable and known radon emanation. Stable emanation power means it is as much independent as possible from the environmental parameters. Since humidity, pressure and temperature can influence the radon emanation property of many of the historical porous materials, they did not meet the requirements of the MetroRadon project. Furthermore, due to aging of these solid porous materials their emanation power degrades in time. It was observed that after 16 years radon emanation changed from few% up to 40% [20]. Long-term chemical and physical stability of MnO_2 coated disks have to be evaluated at JRC in the future.

JRC recently purchased a small size standardised radon emanation chamber with a well-defined geometry that will be used for future experiments. Using this chamber will

enable us to reduce the uncertainty in the air volume and determine the emanation coefficient more accurately. We further plan to investigate the source preparation methods by changing some experimental parameters as listed in Table 2.

Conclusions

JRC-Geel investigated the feasibility of producing drop deposition and chemisorption sources to be used as multi-purpose radon emanation sources suitable as reference emanation sources for ^{222}Rn (radon) with emanations traceable to primary standards.

Both of the emanation source preparation methods proved to be rapid, relatively straightforward and do not require lot of resources. The emanation coefficients for drop deposition- and chemisorption sources varied from 0.10 to 0.74 and from 0.18 to 0.25, respectively. Sources prepared by both methods have their limitations. Further experiments are needed to improve their properties, such as the chemisorption efficiency and emanation power. In addition, the accuracy of the emanation coefficients can be improved by using a standardised radon emanation test environment and comparing chemisorption emanation sources to primary reference emanation sources.

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