Applied Radiation and Isotopes 191 (2023) 110564

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Radon dynamic adsorption coefficients of two activated charcoals at different temperatures in nitrogen environment

Fan Wang [a], Hao Wang [a,b], Hao Ma [c], Lei Zhang [b,*], Changhao Sun [d], Qiuju Guo [a]

[a] State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking University, Beijing, 100871, China
[b] State Key Laboratory of NBC Protection for Civilian, Beijing, 102205, China
[c] Department of Engineering Physics, Tsinghua University, Beijing, 100084, China
[d] Division of Ionizing Radiation Metrology, National Institute of Metrology, Beijing, 100029, China

ARTICLE INFO

Keywords:
Activated charcoal
Radon
Dynamic adsorption coefficient
Temperature dependence
Rare-event search study

ABSTRACT

Profiting from their intrinsic low radioactivity, CarboACT and Saratech, the two kinds of activated charcoal, are commonly adopted in radon removal and radon enrichment process related to modern rare-event search experiments. For supporting CDEX collaboration on radon issue, a flow-through experimental system was established and radon dynamic adsorption coefficients (k_α) of CarboACT and Saratech were systematically measured in N_2 condition within the temperature range of -85 °C~200 °C. The experimental results show that radon dynamic adsorption coefficients of CarboACT and Saratech increase exponentially with the decrease of temperature, and different elution curves of them were observed. Extrapolated to 77K, the k_α-values of CarboACT and Saratech at liquid nitrogen temperature could be firstly estimated at 1.2×10^{13} (L/g) and 9.5×10^{11} (L/g), respectively. The overall image of the adsorption capacities of these two activated charcoals is valuable for rare-event search studies related to radon issue.

1. Introduction

Modern rare-event search experiments mainly include neutrino experiments and dark matter searching experiments, which require ultra-low radioactive measurement background. In the natural radionuclide ^{238}U decay chain, Radon (^{222}Rn) and its progenies are one of the most critical radioactive sources to the background of low energy region. With a half-life of 3.8 days, radon could emanate from all kinds of materials where ^{226}Ra exists, like inner surface of containers, electronics, circulating pumps and detector materials (Aprile et al., 2021). While on the other hand, some core measurement techniques are based on liquid mediums, like liquid xenon (Rupp, 2018) and ultra-pure water (Fukuda et al., 2003). Radon could be dissolved in liquid mediums and distribute almost uniformly in the detector area.

Therefore, radon must be carefully suppressed and determined at an extremely low level in the experiments searching for rare physical processes at low energies, such as Borexino (Alimonti et al., 2009), JUNO (Yu et al., 2021), XENON (Aprile et al., 2017) and XMASS (Abe et al., 2012). For radon removal, activated charcoals with intrinsic low radioactive background are adopted as excellent adsorbents. Radon can be trapped in activated charcoals and decay. For radon measurement, in order to measure radon concentration about $\sim \mu Bq/m^3$ level, radon enrichment by activated charcoals is an effective way to achieve the goal (Guangpeng, 2021). At low temperatures, activated charcoals could adsorb a large number of radon in gas samples, which could be transferred to measurement chamber after heating up the charcoals, and the enrichment of low concentration radon is achieved.

CarboACT (Carboact charcoal specification, 2022) and Saratech (Saratech charcoal specification, 2022), two kinds of commercial activated charcoal, are commonly adopted for radon adsorption and radon removal in low background experiments due to their relatively low intrinsic radiation background, about $0.2 mBq/kg$ and $1.7 mBq/kg$, respectively (Pushkin et al., 2018). In practical applications, radon dynamic adsorption coefficient (k_α) presents the adsorption capacities of activated charcoals, which is influenced by the characteristics of activated charcoals and environmental factors such as air pressure, humidity and temperature (Ronca-Battista and Gray, 1988; Gaul et al., 2005). Radon dynamic adsorption coefficients at different temperatures in different gas environments possess important guiding significance. Hence, up to now, radon dynamic adsorption coefficients of CarboACT and Saratech have been measured in different gas conditions, like N_2, Ar

* Corresponding author.
E-mail address: swofely@pku.edu.cn (L. Zhang).

https://doi.org/10.1016/j.apradiso.2022.110564
Received 21 June 2022; Received in revised form 12 October 2022; Accepted 10 November 2022
Available online 14 November 2022
0969-8043/

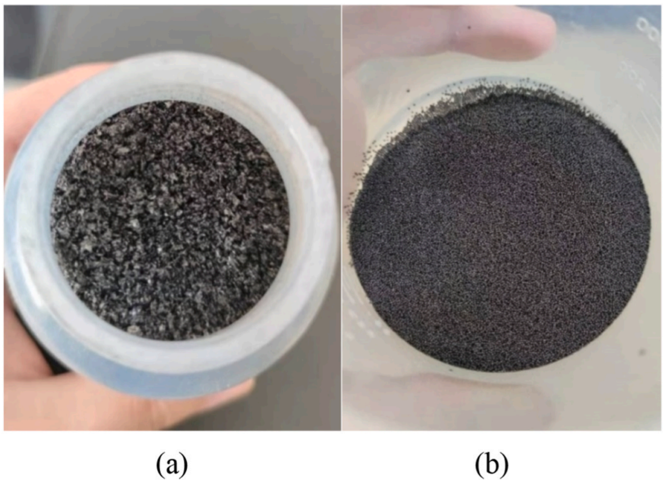

Fig. 1. Photographs of CarboACT (a) and Saratech (b). Measurement system of dynamic adsorption coefficients.

and Xe environment, and at different points of temperature (Pushkin et al., 2018; Wojcik et al., 2017; Chen et al., 2022).

China Dark matter EXperiment (CDEX) is planning to search for weakly interacting massive particles (WIMPs) with a high purity germanium detector array immersed in liquid nitrogen at the China Jinping Underground Laboratory (Jiang et al., 2018; She et al., 2020; Ma et al., 2021). In order to evaluate radiation background, CDEX collaboration plans to use CarboACT and Saratech activated charcoals for the ultra-low-level measurement of radon concentration in liquid nitrogen evaporation gas and radon emanation from materials in liquid nitrogen. For these purposes, it is necessary to understand the entire radon adsorption characteristics of CarboACT and Saratech in nitrogen environment within a wide range of temperature. In this work, we established a flow-through gas system to measure the k_α-values of CarboACT and Saratech systematically in a wider range of temperature compared with previous works.

2. Materials and methods

2.1. Properties of CarboACT and Saratech activated charcoals

Two kinds of activated charcoal, CarboACT and Saratech, were adopted in this study for their inherent low radiation background. CarboACT activated charcoal was purchased from Carbo-act International (Carboact charcoal specification, 2022) at €15000 per kilogram and Saratech activated charcoal was purchased from BLÜCHER PROTECTS (Saratech charcoal specification, 2022) at €40 per kilogram. The photographs of CarboACT and Saratech were shown in Fig. 1. They look significantly different in shape, and detail information of their specific properties is shown in Table 1. As preparation, CarboACT and Saratech were filled in special U-shaped stainless steel tubes in clean room.

On the basis of measurement principle of radon dynamic adsorption coefficient, a flow-through measurement system with activated charcoals in stainless steel tubes was designed and established, as shown in Fig. 2. Before each measurement, CarboACT or Saratech in stainless steel tubes and the gas system were dried by flush of high-purity N_2 for about 30 min. High concentration radon (about $200 Bq/m^3$) was injected at 0.5 standard liters per minute (slpm) for about 2min. High-purity N_2 as carrier gas, supplied by the liquid nitrogen tank (240L) located in the left side of the system, flowed from left to right and carried radon in and out of the U-shaped stainless steel tubes, which was measured by a radon measurement system.

In order to measure the k_α-values at different temperatures, a series of coolers and heaters were used in the gas system. The EK90 Immersion Cooler (Thermo Fisher Scientific, China) (EK90 Immersion Cooler specification, 2022) was used to cool the activated charcoals down to −85 °C and the SDC-6 Cryogenic Bath (NINGBO SCIENTZ BIOTECHNOLOGY, China) (SDC-6 Cryogenic Bath specification, 2022) was used to heat the activated charcoals up to 50 °C. In addition, a heating jacket which was made to order was used to adjust the temperature from 100 °C to 200 °C.

A radon monitor (NARM-P02, Sairatec, China) (NARM-P02 specification, 2022) consisted of an 18 mm × 18 mm Si-PIN photodiode (S3204-09, Hamamatsu Co, Japan) (Hamamatsu Photonics Co, 2022)

Table 1
Properties of CarboACT and Saratech.

Activated charcoal	Shape	Specific activity (mBq/kg)	Bulk density (g/cm^3)	specific surface area (m^2/g)	Particle size (mm)
CarboACT	Fragmented	0.23 ± 0.19 (Pushkin et al., 2018)	0.28 (Carboact charcoal specification, 2022)	800-1200 (Carboact charcoal specification, 2022)	0.0–2.0 (Carboact charcoal specification, 2022)
Saratech	Sphere	1.71 ± 0.20 (Pushkin et al., 2018)	0.60 (Saratech charcoal specification, 2022)	1340 (Saratech charcoal specification, 2022)	0.5–0.8 (Saratech charcoal specification, 2022)

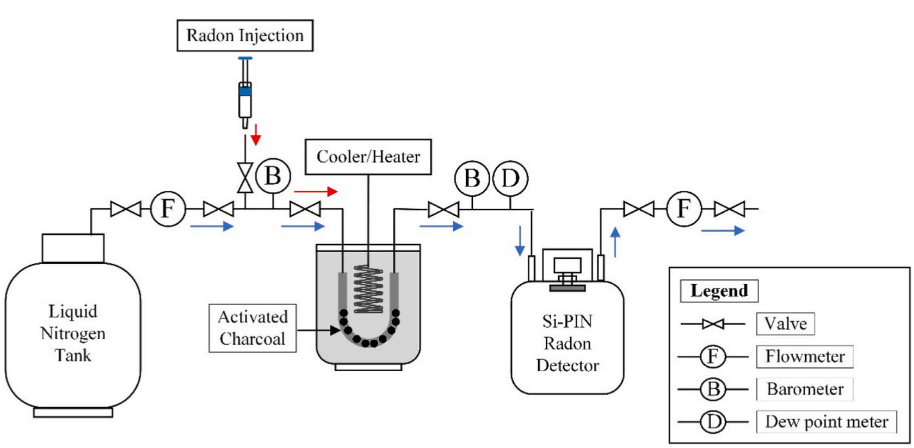

Fig. 2. Schematic diagram of the flow-through system for k_α-values measurement.

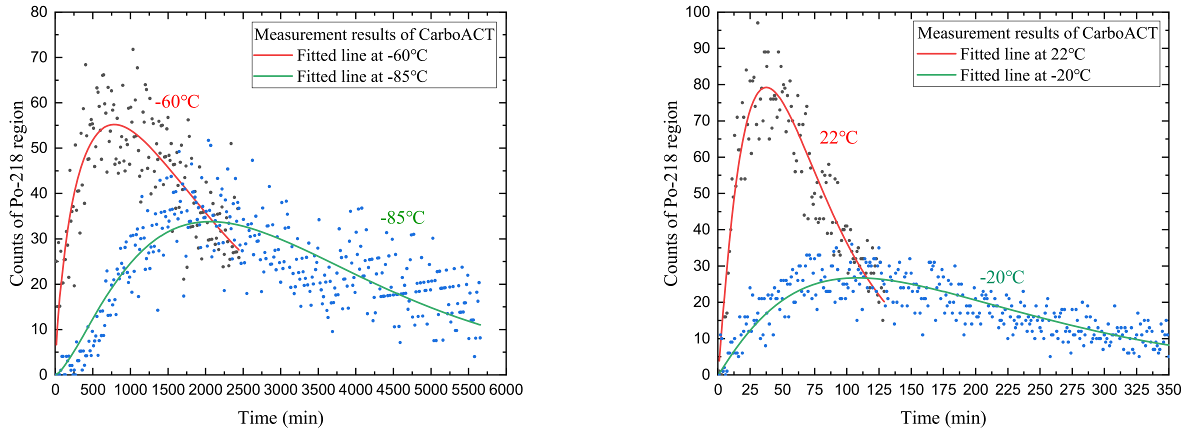

Fig. 3. Alpha-counts of ^{218}Po region and their fitted curves at different temperatures for CarboACT activated charcoal.

and a 20L electrostatic measurement chamber was adopted in this study for continuous measurement on radon concentration at the outlet of the stainless steel tubes. The radon monitor was calibrated by an Alpha-GUARD PQ2000 (Saphymo, France) (Saphymo and Instruments, 2022), which could be traced back to the National Radon Standard of Metrological Institute of China. The typical sensitivity is $21.7cph/(Bqm^{-3})$ and the lower limit of detection is nearly $0.2Bq/m^3$ for 1-h measurement cycle, and the alpha-counts of ^{218}Po (6.00 MeV) is recorded automatically.

During the experiment, the temperature range was set from −85 °C to 200 °C. Aim to reduce the influence of the pressure difference between the two ends of activated charcoals on the measurement results, the gas flow rates were set as low as possible, ranged from 0.6 to 5.1 slpm. The pressure difference was shown by the two barometers at the both ends of the stainless steel tubes. Different masses of activated charcoals were used for measurement in different temperatures and repeated experiments were carried out for two or three times to control the measurement quality.

2.2. Calculation of dynamic adsorption coefficients

There are mainly two methods of measuring the dynamic adsorption coefficients of activated charcoals: injected gas inlet (Pushkin et al., 2018) and continuous gas inlet (Guo et al., 2017). Considering the difference of accuracy, the method of injected gas inlet was adopted in this study, that was, after a single injection of radon, the radon concentration at the outlet of the activated charcoals was measured continuously. According to the HETS model, the radon concentration at the outlet of activated charcoals should be expressed as follows (Golightly, 2008):

$$C_{output}(t) = \frac{An^n}{(n-1)!}\left(\frac{t}{\tau}\right)^{n-1} e^{-\frac{nt}{\tau}} \tag{1}$$

Where A is scale factor (Bq/m^3), τ is the breakthrough time (min) of ^{222}Rn in a carrier gas, and n is the number of theoretical stages. The values of τ could be achieved through fitting the alpha-counts of ^{218}Po time series data measured by the radon detector with formula (1). The values of radon dynamic adsorption coefficients are finally given as follows:

$$k_a = \frac{\tau\Phi}{m} \tag{2}$$

Where Φ is flow rate (slpm) and m is the mass (g) of activated charcoal.

3. Results and discussion

3.1. The measurement curves of activated charcoals at different temperatures

The alpha-counts of ^{218}Po region over time and their fitted curves according to formula (1) at 22 °C, −20 °C, −60 °C and −85 °C are shown in Figs. 3 and 4, respectively. We can observe significant different elution curves between the two kinds of activated charcoal, and between different temperatures as well. In general, radon leaked out of CarboACT immediately after the carrier gas flowed. While as a contrast, Saratech could trap radon in the initial period of time. In addition, radon concentration at the outlet of CarboACT decreased more slowly.

The different elution curves of CarboACT and Saratech in Figs. 3 and

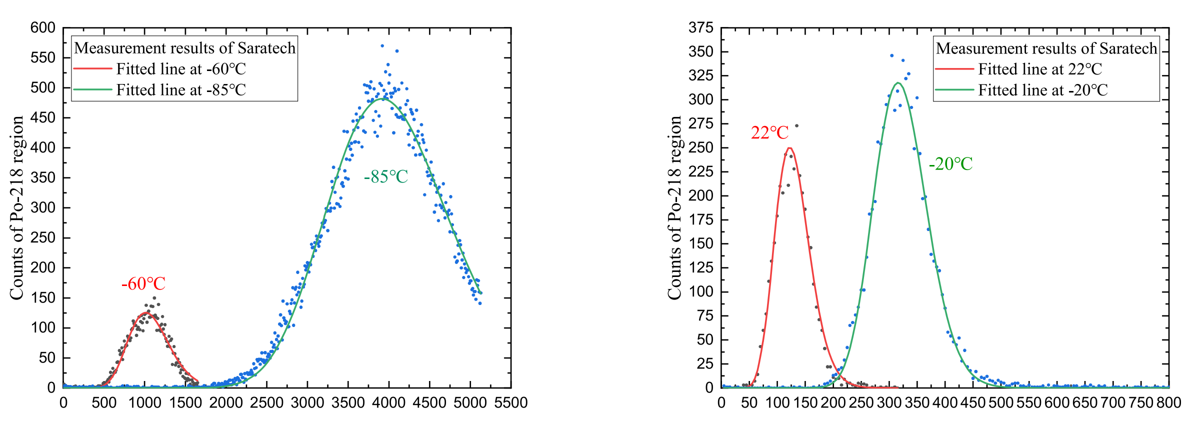

Fig. 4. Alpha-counts of ^{218}Po region and their fitted curves at different temperatures for Saratech activated charcoal.

Table 2
Experimental parameters and results of CarboACT.

Temperature (K/°C)	Mass(g)	Flow rate (slpm)	Pressure difference (kPa)	Breakthrough time τ (min)	Theoretical stages n	Dynamic adsorption coefficient (L/g)
473 (200 °C)	20.0	0.6	0.7	14.7	3.8	0.4 ± 0.1
373 (100 °C)	20.0	1.0	1.0	28.4	3.5	1.4 ± 0.1
323 (50 °C)	20.0	2.0	1.8	36.2	2.0	3.6 ± 0.3
295 (22 °C)	20.0	3.1	3.4	70.6	2.1	10.9 ± 0.8
273 (0 °C)	20.0	1.9	1.3	239.9	2.2	22.7 ± 1.8
253 (-20 °C)	10.0	3.4	5.2	205.2	2.1	69.6 ± 4.7
233 (-40 °C)	4.4	3.0	11.0	406.9	2.8	272 ± 19
213 (-60 °C)	4.4	2.1	8.0	1891	1.7	900 ± 96
188 (-85 °C)	3.0	2.1	6.5	3411	2.5	2380 ± 240

Table 3
Experimental parameters and results of Saratech.

Temperature (K/°C)	Mass (g)	Flow rate (slpm)	Pressure difference (kPa)	Breakthrough time τ (min)	Theoretical stages n	Dynamic adsorption coefficient (L/g)
473 (200 °C)	60.0	2.0	8.2	13.2	7.4	0.4 ± 0.1
373 (100 °C)	60.0	2.2	8.4	27.7	18.2	1.0 ± 0.1
323 (50 °C)	60.0	2.1	8.1	54.2	17.4	1.9 ± 0.1
295 (22 °C)	60.0	2.6	9.0	130.1	17.0	5.6 ± 0.4
273 (0 °C)	60.0	2.9	9.6	327.4	9.8	15.8 ± 1.1
253 (-20 °C)	20.0	2.2	4.1	323.0	45.9	35.4 ± 2.6
233 (-40 °C)	20.0	3.4	7.0	531.6	28.2	89.0 ± 5.8
213 (-60 °C)	20.0	5.1	9.9	1075	17.7	275 ± 19
188 (-85 °C)	20.0	4.6	10.0	4056	29.0	937 ± 67

Table 4
Comparison of measurement results for Saratech with previous works.

Temperature (°C)	Dynamic adsorption coefficient (L/g)		
	This work, 2022	K. Pushkin et al., 2018	Y.Y. Chen et al., 2022
22 °C	5.6 ± 0.4	5.4 ± 0.3	\
0 °C	15.8 ± 1.1	13 ± 1	\
−20 °C	89.0 ± 5.8	33 ± 2	\
−60 °C	275 ± 19	\	167.1 ± 2.1

4 might be attributed to their different shapes of the charcoal particles. The shape and the particle size of Saratech are more uniform than those of CarboACT, which are showed in Table 1 and Fig. 1. In the process of filling the activated charcoals into the stainless steel tubes, we noticed that Saratech is more compact than CarboACT in tubes because of its uniform shape, which leads to less space between charcoal particles. Thus, for Saratech, the ratio of adsorption surface area to its volume is larger, resulting in significant greater theoretical stages n (detail information in Table 2 and Table 3). According to formula (1), they would take the different forms of curves in Figs. 3 and 4. Moreover, in the work of K. Pushkin et al. (2018), for different activated charcoals with different fitted curves, similar explanation was given.

3.2. The dynamic adsorption coefficients at different temperatures

Radon dynamic adsorption coefficients of CarboACT and Saratech at nine points of temperature were measured individually. Information of experimental parameters and their relative results are shown in Tables 2 and 3. When temperature increased from −85 °C to 200 °C, the k_α-values of CarboACT are decreased from $(2380 \pm 240)L/g$ to $(0.4 \pm 0.1)L/g$ and the k_α-values of Saratech are decreased from $(937 \pm 67)L/g$ to $(0.4 \pm 0.1)L/g$. In general, the k_α-values of activated charcoals decreased exponentially with the increase of temperature.

Compared with previous works, the measurement results of Saratech activated charcoal are quite consistent with radon dynamic adsorption coefficients at −20 °C, 0 °C and 22 °C reported by K. Pushkin et al. (2018), but significantly greater than those at −60 °C in the paper of Y.Y. Chen et al. (2022) (continuous gas inlet), as shown in Table 4. As for CarboACT, no previous measurement results in nitrogen environment have been reported.

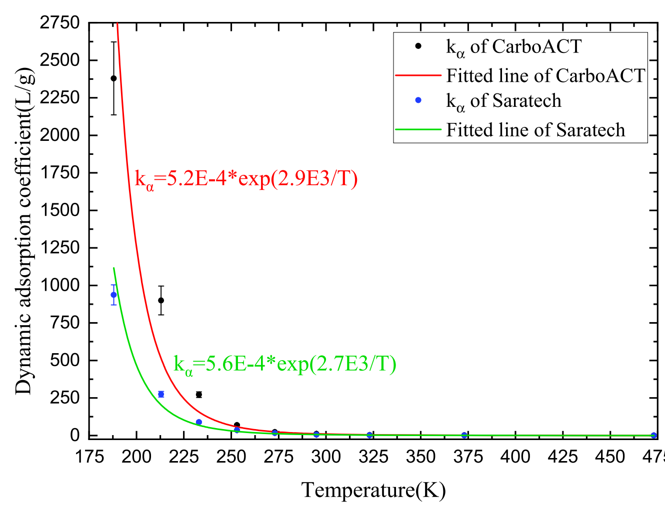

Fig. 5. Functional relationship of CarboACT and Saratech between k_α and T.

3.3. Fitting results of dynamic adsorption coefficients at different temperatures

In Adamson's work (Adamson, 1990), k_α is a function of absolute temperature T and adsorption heat Q, and the functional relationship is expressed as follows:

$$k_\alpha = k_0 e^{\frac{Q}{RT}}$$

Where R is molar gas constant ($R = 8.3149J/(mol \bullet K)$) and k_0 is scale factor. The relationship between k_α and temperature T is fitted according to the above formula, which is shown in Fig. 5. The fitting results give the adsorption heat Q of CarboACT and Saratech:

$$Q_{CarboACT} = 2.4 \times 10^4 (L/mol)$$

$$Q_{Saratech} = 2.2 \times 10^4 (L/mol)$$

The adsorption heat Q reflects the adsorption capacity of activated charcoals. Since CarboACT possesses higher adsorption heat, its radon dynamic adsorption coefficients are significantly greater than those of Saratech, especially at low temperatures.

Due to the experimental requirements of CDEX collaboration, radon dynamic adsorption coefficients of CarboACT and Saratech at liquid nitrogen temperature (−196 °C/77K) are essential factors to be known. In practice, however, limited by measurement conditions, the k_α-values of them at 77K are usually estimated through extrapolation. In this work, they are calculated to be $k_\alpha^{CarboACT}(77K) = 1.2 \times 10^{13}(L/g)$ and $k_\alpha^{Saratech}(77K) = 9.5 \times 10^{11}(L/g)$, respectively. These results are nearly at the same order of magnitude as those given in the paper of M. Wojcik et al. (2017).

4. Conclusion

For modern rare-event search experiments in underground laboratories worldwide, radon removal and ultra-low-level measurement are shared challenges. To solve this problem, activated charcoals, especially CarboACT and Saratech, become common choices owing to their rather lower radiation background. Hence, the exact adsorption behaviors of them should be known clearly. Based on the requirement of CDEX collaboration, the k_α-values of CarboACT and Saratech activated charcoals were systematically measured in nitrogen environment and the overall image of their adsorption characteristic was given in detail by this work, which could offer instructions in the future practical application of CDEX.

Considering the experimental cost, CarboACT activated charcoal is much more expensive than Saratech activated charcoal. In practical application, CarboACT is more suitable for radon enrichment due to its lowest intrinsic radiation background, and Saratech has superiority in radon removal for its lower price. For different experimental requirements, the type, mass and operating temperature of activated charcoals should be selected reasonably.

CRediT authorship contribution statement

Fan Wang: Writing – review & editing, Writing – original draft, Methodology, Data curation. **Hao Wang:** Supervision, Investigation, Conceptualization. **Hao Ma:** Writing – review & editing, Funding acquisition. **Lei Zhang:** Writing – review & editing, Project administration, Methodology, Investigation, Conceptualization. **Changhao Sun:** Investigation, Conceptualization. **Qiuju Guo:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

We would like to thank the financial support of the State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking University and the National Natural Science Foundation of China (No.12275008).

References

Abe, K., et al., 2012. Radon removal from gaseous xenon with activated charcoal. Nucl. Instrum. Methods A 661, 50. https://doi.org/10.1016/j.nima.2011.09.051.
Adamson, A., 1990. Physical Chemistry of surfaces[M] (New York).
Alimonti, G., et al., 2009. The Borexino detector at the Laboratori Nazionali del Gran Sasso. Nucl. Instrum. Methods A 600, 568. https://doi.org/10.1016/j.nima.2008.11.076.
Aprile, E., et al., 2017. The XENON1T dark matter experiment. Eur. Phys. J. C 77, 881. https://doi.org/10.1140/epjc/s10052-017-5326-3.
Aprile, E., et al., 2021. ^{222}RnEmanation measurements for the XENON1T experiment. Eur. Phys. J. C 81, 337. https://doi.org/10.1140/epjc/s10052-020-08777-z.
Carboact charcoal specification. https://www.carboactinternational.com/. (Accessed 18 August 2022). Last time accessed.
Chen, Y.Y., et al., 2022. A study on the radon removal performance of low background activated carbon. J. Inst. Met. 17, P02003 https://doi.org/10.1088/1748-0221/17/02/P02003.
EK90 Immersion Cooler specification. https://assets.thermofisher.cn/TFS-Assets/LED/manuals/EK45-EK90-immersion-coolers-manual-multilingual.pdf. (Accessed 18 August 2022). Last time accessed.
Fukuda, S., et al., 2003. The Super-Kamiokande detector. Nucl. Instrum. Methods A 501, 418. https://doi.org/10.1016/S0168-9002(03)00425-X.
Gaul, et al., 2005. Dynamic adsorption of radon by activated carbon. Health Phys. 88, 371–378. https://doi.org/10.1097/01.HP.0000152110.01409.3e.
Golightly, J., 2008. Characterization of a Carbon Radon Filter, and Radon detection[D]. Queen's University, pp. 61–65.
Guangpeng, A.N., 2021. Study of low temperature radon removal Technology and low background radon measurement in nitrogen[J]. Nucl. Phys. Rev. 38 (2), 175–181. https://doi.org/10.11804/NuclPhysRev.38.2020063.
Guo, Lu, et al., 2017. The temperature dependence of adsorption coefficients of ^{222}Rnon activated charcoal: an experimental study. Appl. Radiat. Isot. 125, 185–187. https://doi.org/10.1016/j.apradiso.2017.04.023.
Hamamatsu Photonics Co, https://www.hamamatsu.com/, Last time accessed: 2022-8-18.
Jiang, H., et al., 2018. Limits on light weakly interacting massive particles from the first 102.8 kg × day data of the CDEX-10 experiment. Phys. Rev. Lett. 120, 241301 https://doi.org/10.1103/PhysRevLett.120.241301.
Ma, H., et al., 2021. Status and prospect of China jinping underground laboratory. J. Phys.: Conf. Ser. 2156, 012170 https://doi.org/10.1088/1742-6596/2156/1/012170.
NARM-P02 specification. http://www.sairatec.com/teamview_5999934.html. (Accessed 18 August 2022). Last time accessed.
Pushkin, K., et al., 2018. Study of radon reduction in gases for rare event search experiments. Nucl. Instrum. Methods A903, 267. https://doi.org/10.1016/j.nima.2018.06.076.
Ronca-Battista, M., Gray, D., 1988. The influence of changing exposure conditions on measurements of radon concentrations with the charcoal adsorption technique. Radiat. Protect. Dosim. 24, 361–365. https://doi.org/10.1093/oxfordjournals.rpd.a080303.
Rupp, N., 2018. Radon background in liquid xenon detectors. J. Inst. Met. 13, C02001 https://doi.org/10.1088/1748-0221/13/02/C02001.
Saphymo, Instruments, Bertin. https://www.saphymo.com. (Accessed 18 August 2022). Last time accessed.
Saratech charcoal specification. https://www.bluecher.com/en/. (Accessed 18 August 2022). Last time accessed.
SDC-6 cryogenic Bath specification. https://www.scientz.com/products/335.html. (Accessed 18 August 2022). Last time accessed.
She, Z., et al., 2020. Direct detection constraints on dark photons with the CDEX-10 experiment at the China jinping underground laboratory. Phys. Rev. Lett. 124 (11), 111301 https://doi.org/10.1103/PhysRevLett.124.111301.
Wojcik, M., et al., 2017. Review of high-sensitivity Radon studies. Int. J. Mod. Phys. 32, 1743004 https://doi.org/10.1142/S0217751X17430047.
Yu, X., et al., 2021. Nitrogen purification pilot plant of Jiangmen underground neutrino observatory. J. Inst. Met. 16, T08002 https://doi.org/10.1088/1748-0221/16/08/T08002.