



Analysis of the ^{222}Rn concentration in argon and a purification technique for gaseous and liquid argon

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ABSTRACT

We present an investigation of the ^{222}Rn concentration in argon with ultra-low background proportional counters. Argon purification tests by means of cryo-adsorption of radon on activated carbon were performed. For gaseous argon the purification process was found to be very efficient. Also in liquid phase the ^{222}Rn concentration could be reduced significantly, however, the efficiency is lower than in the gas phase. We also have analyzed the initial ^{222}Rn concentrations in commercial liquid argon. It was found to be significantly higher than in liquid nitrogen.

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1. Introduction

Liquefied noble gases are of growing importance for astroparticle physics experiments looking for very few events at low energies. This is mainly because they are excellent scintillators with high light yield, thus providing good energy resolution and a low detection threshold. At the same time they can be used as liquid passive shield with relatively high density (e.g. compared to water or liquid nitrogen). Argon is particularly interesting, as it is relatively cheap and abundantly available. The tolerable background rates in this kind of experiments are extremely low, e.g. $10^{-3} (\text{keV kg a})^{-1}$ around 2 MeV in the GERDA double beta decay experiment (Abt et al., 2004). Therefore, argon must have extremely low radioactive contamination. Most dangerous is the radioactive noble gas isotope ^{222}Rn (3.82 days half-life DDEP, 2008), which is not only present at high concentrations in the atmosphere, but is also emanated from materials containing ^{226}Ra , a successor of primordial uranium. Since in the ^{222}Rn decay chain alpha-, beta- and gamma-decays are present over a wide range of energy, it is dangerous for essentially any low energy rare event experiment. ^{220}Rn is usually less problematic because of its short half-life (55.8 s (DDEP, 2008)). In this work we present a ^{222}Rn purification technique for gaseous and liquid argon as well as a survey of the ^{222}Rn concentrations in commercially available liquid argon.

2. Experimental techniques

Ultra-low background proportional counters, which were developed for the GALLEX solar neutrino experiment (Wink et

al., 1993) are used to detect ^{222}Rn in small gas samples. The combined detection efficiency for the three subsequent alpha-decays from ^{222}Rn to the long-lived ^{210}Pb is $(147 \pm 6)\%$ due to wall effects, field imperfections at the cathode edges and the unavoidable geometrical dead volume in the hand-made proportional counters. The background varies for individual counters and lies between 0.05 and a few counts per day for an energy threshold of 50 keV. A thorough preparation of any gas sample is necessary to avoid radioactive impurities and electro-negative gases, which would diminish the performance of the counters. This is done with a low background gas handling and proportional counter filling system made out of glass. The blank contribution of the system lies around $6 \mu\text{Bq}$ for a single run. Therefore, the minimal detectable activity depends mostly on the counter used and lies around a few tens of μBq .

To collect ^{222}Rn from large amounts of argon an apparatus called MoREx (Mobile Radon Extraction unit (Heusser et al., 2000)) was used. It mainly consists of two columns filled with 150 g of the high-purity activated carbon CarboAct™ that can be operated at low temperature. It is not possible to transfer radon from such large carbon columns directly to the gas handling system mentioned above. Therefore, the sample is first transferred from the 150 g column to a 10 g CarboAct™ column. The whole process introduces a ^{222}Rn activity of another few tens of μBq . However, samples up to several 100 m^3 (at Standard Temperature and Pressure (STP)) can be processed with MoREx, so a minimum detectable activity concentration of less than $1 \mu\text{Bq m}^{-3}$ (STP) can be obtained.

MoREx is designed only for gas phase operations. Liquid phase purification tests have to be done by dedicated different systems. We have developed two activated carbon columns of different mass with dedicated instrumentation for liquid phase operations. They feature an electrical heater to evaporate the argon, so that they can be put in series with MoREx for combined

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liquid/gas phase analyses. Fig. 1 shows a simplified sketch of the setup.

3. Purification tests

3.1. Gas phase purification

For the gas phase purification tests liquid argon was evaporated and warmed up to a temperature around 30 °C. Then it was led through the first of the two MoREx activated carbon columns which was cooled down to –186 °C by immersing it in liquid argon. The chosen mass flow rate of ~25 kg h⁻¹ provided a sufficiently high gas speed to avoid re-liquefaction of the argon in the column. The observed temperature at the exit of the carbon column was about –170 °C. After another warming up the argon enters the second column which is also immersed in liquid argon. By comparing the amount of ²²²Rn trapped in the respective column the purification factor can be derived. Due to the low detection limit of our technique the ²²²Rn concentration in commercial argon is sufficiently high to avoid an artificial spiking with ²²²Rn.

Two gas phase purification tests were performed, one processing 80 m³ (STP) and one processing 141 m³ (STP) of argon. In both cases no ²²²Rn could be found in the second column. Thus, only lower limits for the reduction factors can be quoted. In the first case we found a reduction factor larger than 360 while in the second case a lower limit of 1120 was obtained. These limits have a coverage factor of $k = 1.645$, representing approximately 90% probability. The results can also be quoted in a different way: If we

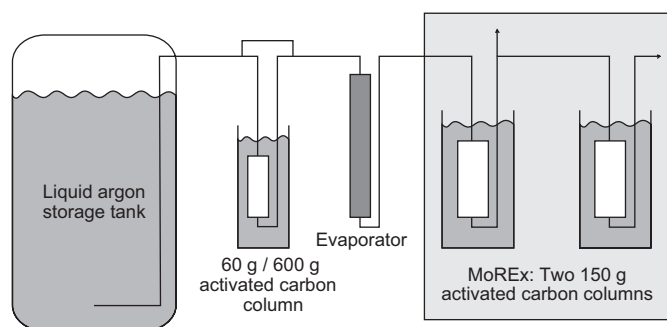


Fig. 1. Sketch of the setup used for the purification measurements. For gas phase tests the first column was bypassed and only the two 150 g activated carbon columns of MoREx were used. For liquid phase measurements only one of the MoREx columns was used. See the text for further explanations.

assume that the ²²²Rn concentration in the argon behind the first carbon column is constant during a run it is possible to quote an upper limit for it. With that assumption the result for the ²²²Rn concentration in the purified argon is <0.7 μBq m⁻³ (STP) for the first run and <0.2 μBq m⁻³ (STP) for the second run.

3.2. Liquid phase purification

If large amounts of purified liquid argon have to be produced it is inconvenient and expensive to do the purification in the gas phase due to the necessary evaporation and re-condensation process. Therefore, we have investigated the liquid phase purification process. The first series of measurements were performed with a 60 g CarboAct™ column as liquid phase purifier. Again the carbon column was immersed in liquid argon to maintain low temperature. The liquid argon for the purification test was taken from a cryogenic storage tank, which was connected with a relatively short flexible stainless steel tube to the carbon column. At the chosen flow rate of ~25 kg h⁻¹ the heat input by this setup was sufficiently low to maintain a large fraction of the argon inside the column in the liquid phase. To analyze the residual ²²²Rn concentration in the purified liquid argon, we evaporated it and used one of the MoREx activated carbon columns as a gas phase analyzer. The gas phase purification tests have shown that the efficiency of this process is compatible with 100%. Thus, the leaking fraction (the inverse of the purification factor) through the 60 g column can be obtained by dividing the amount of ²²²Rn found in the MoREx column by the sum of the ²²²Rn in the 60 g and in the MoREx column. In a second campaign we replaced the 60 g column by a 600 g column (again filled with CarboAct™) and repeated the measurements. Table 1 summarizes the obtained results for different amounts of processed liquid argon. Due to the relatively low count rates statistical uncertainties dominate over systematic effects. Thus, all uncertainties are given as standard uncertainties with 68% level of confidence.

From the theoretical point of view the activated carbon column acts as a chromatography column with a different traveling speed of the carrier gas (argon) and the contaminant (²²²Rn). According to the model of column chromatography a characteristic breakthrough curve is expected behind the column. The moment when the ²²²Rn concentration in the purified argon is reached 50% of its initial value is known as the retention time. It is directly related to the strength of the adsorption forces between the contaminant and the adsorber. For more detailed information the reader is referred for example to (Simgen, 2005). However, in practice the

Table 1

Summary of the purification results for liquid argon purification from ²²²Rn with two different activated carbon columns (60 g and 600 g).

Carbon mass (g)	Processed LAr (liter)	²²² Rn activity (mBq)			Leaking fraction (%)
		Column 1	Column 2	Sum	
60	58	6.9 ± 0.5	0.12 ± 0.03	7.0 ± 0.5	1.7 ± 0.5
60	120	5.0 ± 0.3	0.17 ± 0.05	5.2 ± 0.3	3.3 ± 1.1
60	120	5.6 ± 0.5	0.21 ± 0.05	5.8 ± 0.5	3.6 ± 0.9
60	125	10.8 ± 0.7	0.54 ± 0.06	11.3 ± 0.7	4.8 ± 0.6
60	168	28.1 ± 2.1	0.68 ± 0.08	28.8 ± 2.1	2.4 ± 0.3
60	188	12.7 ± 0.7	1.70 ± 0.19	14.4 ± 0.8	11.8 ± 1.5
60	193	122 ± 8	31.2 ± 3.3	153 ± 8	20.4 ± 2.4
60	222	59.8 ± 3.9	0.38 ± 0.06	60.0 ± 3.9	0.6 ± 0.1
60	240	1080 ± 40	120 ± 6	1200 ± 40	9.9 ± 0.6
600	76	10.3 ± 0.7	0.19 ± 0.04	10.5 ± 0.7	1.8 ± 0.4
600	237	0.9 ± 0.1	0.12 ± 0.03	1.0 ± 0.1	12.1 ± 3.6
600	244	64.7 ± 2.9	0.24 ± 0.05	64.9 ± 2.9	0.4 ± 0.1

All uncertainties are standard uncertainties with 68% level of confidence.

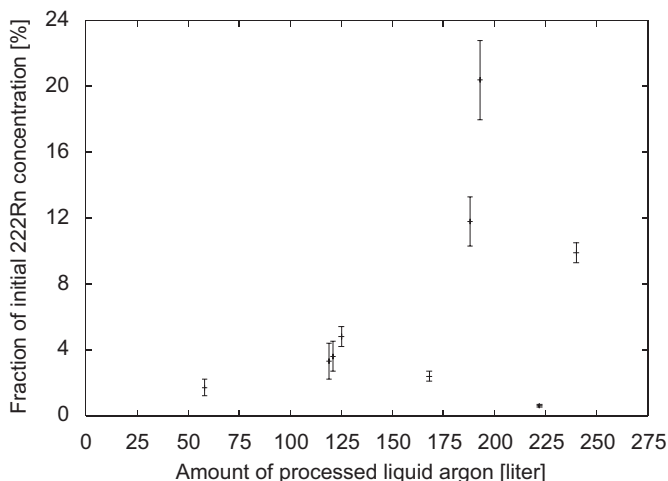


Fig. 2. The fraction of ^{222}Rn leaking through the 60 g activated carbon adsorption column as a function of the processed amount of liquid argon. The error bars represent standard uncertainties with 68% level of confidence.

^{222}Rn concentration in the purified argon will never be exactly zero. Even at the very beginning a minor fraction of ^{222}Rn passes through the column without participating in the adsorption process. This reflects the fact that a contaminant can only be adsorbed if it reaches appropriate adsorption pores by diffusion. This diffusion process takes a finite time so that the contaminant may leave the column before it can be adsorbed for the first time. In the data the fraction of non-adsorbed contaminants will show up as an offset in the breakthrough curve. The height of the offset probably depends on the size and structure of channels, which form during a run between the adsorber grains.

Fig. 2 shows the obtained data for the 60 g column as a function of the processed liquid argon volume. Neither a constant offset nor a breakthrough curve can be clearly recognized. Instead, the scattering of the data points is large and indicates substantial systematic contributions to the uncertainties. It should be noted that these systematic effects are due to varying conditions between the runs. The uncertainties within a run are still dominated by statistical uncertainties. In spite of the scattering, the leaking fraction of ^{222}Rn is 10% or less for most of the data points. This shows that ^{222}Rn removal from liquid argon is possible, although the efficiency is significantly lower than for gaseous argon. The difference between liquid phase and gas phase adsorption is expected due to the much lower mobility of radon in liquefied argon. Therefore, the diffusion to appropriate adsorption pores is slower resulting in weaker purification ability.

The question whether the observed data represents only an offset or the beginning of a real breakthrough through the column is crucial for later applications. Since an offset is constant in time it is possible to use the same column for purification of more liquid argon with the same reduction factor. On the other hand, if a breakthrough starts, the ^{222}Rn concentration will continue to increase and the column can no longer be used without regeneration. Although the data do not allow a clear distinction between the two scenarios there is a hint for the case of an offset: The two data points at 120 liter liquid argon were taken at two different pressures (4.5 bar overpressure and 1 bar overpressure, respectively). Consequently, the temperature of the liquefied argon was different by more than 10 °C. The strength of the adsorption forces depends in an exponential manner on the temperature. Therefore, at elevated temperatures the adsorption forces should be much weaker resulting in a much larger leaking fraction. Since both data points show almost the same reduction factor the scenario of a breakthrough is disfavored.

Table 1 contains also results obtained with a larger activated carbon column (600 g). Here, the fraction leaking through the column lies between 0.4% and 1.8% except for one measurement for which 12% was found. However, in the 12% case the initial ^{222}Rn concentration was accidentally very low so that a non-negligible influence of the ^{222}Rn -emanation from the experimental setup is expected which is most likely responsible for the poor result.

The liquid phase purification results show a heterogeneous picture. On the one hand a clear reduction of the ^{222}Rn concentration is visible. It is also evident that the purification efficiency is lower than for the gas phase purification. On the other hand the uncertainties are dominated by systematic effects making the interpretation of the results difficult. Possible reasons are non-stable operation conditions (fluctuating temperature/pressure/flux), poorly known blank contributions and large differences in the number and structure of channels which form during a run. Our setup will be upgraded in the near future to provide stable conditions by automatic controlling of the relevant parameters. This allows also processing even larger samples. Both effects will help to minimize systematic uncertainties and eventually to unambiguously distinguish between offset- and breakthrough-scenario.

4. Survey of commercially available argon

Since in all performed purification tests the second activated carbon column was operated in the gas phase, no or negligibly little ^{222}Rn was lost during a measurement. Therefore, it is possible to extract from the purification data the absolute ^{222}Rn concentration in the argon. The liquid argon was delivered either in a rental storage container or it was loaded from a truck in a permanently installed storage tank. In the second case the argon was taken directly from an air separation plant while in the first case it was taken from a local distribution center of the supplier where it was stored before for an unknown time. Since ^{222}Rn decays within a few days it is crucial to take into account the time between the measurement on the one hand and the production (or delivery) on the other hand. We have determined the initial ^{222}Rn concentration in nine different batches of liquid argon from three suppliers (Air Liquide, Westfalen AG, Linde). The results are summarized in Table 2. The upper part represents the samples with intermediate storage while the lower part shows the samples that are coming directly from the air separation plant. Usually, the moment when the argon leaves the supplier's site is the reference time. For the argon from Linde this time is not known, so the delivery time is used instead. We therefore remark that the concentration at the time of production was a little higher.

The results vary by three orders of magnitude from $(7 \pm 1) \mu\text{Bq m}^{-3}$ (STP) to $(8.4 \pm 0.4) \text{mBq m}^{-3}$ (STP). The variations in the upper part of Table 2 may be explained by the different unknown storage times in the local distribution center. During the storage initial ^{222}Rn decays while new ^{222}Rn is accumulated due to leaks, emanation from tank walls or other impurities. Therefore, the results cannot be compared directly. Within the samples coming directly from the air separation plant we procured one batch of high purity liquid argon (grade 6.0) from Westfalen AG. It is more than one order of magnitude purer than the technical quality argon from the same supplier. However, the Linde technical quality argon is much lower in ^{222}Rn than the Westfalen AG technical quality argon. Although we do not know the exact reference time for the Linde sample, its initial activity cannot be as high as the Westfalen AG technical quality sample, since the argon usually leaves the air separation plant not more than a few days before the delivery.

Table 2

Measured ^{222}Rn concentration in commercial argon at the time when the argon leaves the supplier's site.

Supplier	Grade	Initial ^{222}Rn activity (mBq m^{-3} (STP))
Air Liquide	Technical (4.8)	1.62 ± 0.08
Air Liquide	Technical (4.8)	0.38 ± 0.03
Westfalen AG	Technical (4.6)	1.11 ± 0.05
Westfalen AG	Technical (4.6)	1.04 ± 0.09
Westfalen AG	Technical (4.6)	0.50 ± 0.02
Westfalen AG	Technical (4.6)	0.007 ± 0.001
Westfalen AG	Technical (5.0)	8.4 ± 0.4
Westfalen AG	High purity (6.0)	0.38 ± 0.01
Linde	Technical (5.0)	0.37 ± 0.06^a

The samples in the upper part of the table were stored for an unknown time in a local distribution center of the supplier. The samples in the lower part were delivered directly from the respective air separation plant. All uncertainties are standard uncertainties with 68% level of confidence.

^a At the time of delivery.

In general most of the concentrations lie in the mBq m^{-3} (STP) range. This is about 10 times larger than the measured ^{222}Rn concentrations in technical quality liquid nitrogen (Heusser et al., 2000). This effect can be explained as follows: In air separation plants gases are separated by fractionated distillation according to their boiling points. The boiling point of argon is somewhat closer to radon than the boiling point of nitrogen. Therefore, it is likely that residual atmospheric ^{222}Rn in freshly produced argon is somewhat enriched with respect to freshly produced nitrogen.

5. Conclusions

We have used ultra-low background proportional counters to study the ^{222}Rn contamination in commercial argon. The initial

concentration usually lies in the range of mBq m^{-3} (STP) with strong fluctuations. This is about one order of magnitude higher than in nitrogen. We have proven that gaseous argon can be purified efficiently from ^{222}Rn by cryo-adsorption on activated carbon. ^{222}Rn concentration reductions of more than a factor 1000 were achieved. We have also performed liquid phase purification tests with activated carbon columns of two different sizes (60 g and 600 g). The results suffer from systematic uncertainties, but in most cases the ^{222}Rn concentration could be reduced by more than a factor 10. This makes us confident that with sufficiently large activated carbon columns an efficient purification of argon is possible on a large scale without prior transformation to the gas phase.

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