$^{222}$Rn detection at the $\mu$Bq/m$^3$ range in nitrogen gas and a new Rn purification technique for liquid nitrogen

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Abstract

For the Borexino solar neutrino experiment a concentration line for $^{222}$Rn from a large volume of nitrogen gas has been constructed. It is based on cryo-adsorption in a charcoal trap of very low intrinsic $^{226}$Ra contamination. Consequently, the blank for activity from the daughter nuclide $^{222}$Rn is very low. $^{222}$Rn is recorded with proportional counters. This allows the detection of Rn at concentrations below the $\mu$Bq/m$^3$ level in gaseous nitrogen.

The removal of radon from liquid nitrogen is achieved by direct adsorption in the liquid phase. $^{222}$Rn – measurements on evaporated nitrogen with and without previous purification are reported. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Solar neutrino detection in the Borexino experiment (Arpesella et al., 1991) by elastic neutrino electron scattering in 300 ton (100 ton fiducial volume) of liquid scintillator requires extreme radiopurity. The most challenging prerequisite is the $^{222}$Rn-purity of the scintillator. Purification is achieved by gas stripping using nitrogen. For this purpose the nitrogen must not contain more than some $\mu$Bq/m$^3$ of $^{222}$Rn. Also for other operations nitrogen gas of such purity is needed in the experiment. The Borexino experiment is being under construction at the Gran Sasso Underground Laboratory.

So far, present day state of the art techniques for Rn-monitoring were short for this purpose by at least two orders of magnitude, even if preconcentration is applied. However, a major effort allowed achieving this goal. A concentration line was built in order to isolate Rn from several 100 m$^3$ of nitrogen gas while, at the same time, the blank activity that was accumulated from sources other than nitrogen remained at a tolerable level. The activity measurement is performed by internal gas counting with miniature proportional counters. They were originally developed for the solar neutrino experiment GALLEX, see e.g. (Wink et al., 1993).

The Rn concentration in nitrogen gas that evolved from standard liquid nitrogen turned out to be higher than the level required. Therefore, a charcoal purification column system was constructed to adsorb Rn
Table 1
Radionuclide concentration of some charcoal samples, measured by Ge low level gamma spectrometry. Typical sample size was 19–60 g. $^{222}\text{Rn}$ was measured after heat extraction in gas counters

<table>
<thead>
<tr>
<th>Charcoal sample</th>
<th>Specific activity (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{137}\text{Cs}$</td>
</tr>
<tr>
<td>Silcarbon Sil40</td>
<td>$\leq 1$</td>
</tr>
<tr>
<td>Silcarbon C46</td>
<td>$1.2 \pm 0.2$</td>
</tr>
<tr>
<td>Silcarbon K48</td>
<td>$\leq 1$</td>
</tr>
<tr>
<td>Hydraulin CC8x30</td>
<td>$1.3 \pm 0.2$</td>
</tr>
<tr>
<td>Hydraulin UV43</td>
<td>$3.4 \pm 0.2$</td>
</tr>
<tr>
<td>Model PCB616</td>
<td>$5.3 \pm 0.3$</td>
</tr>
<tr>
<td>Model 1193</td>
<td>$0.6 \pm 0.1$</td>
</tr>
<tr>
<td>Alcarbon 12x20</td>
<td>$0.1 \pm 0.06$</td>
</tr>
<tr>
<td>Alcarbon 7x16</td>
<td>$1.5 \pm 0.2$</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>$\leq 0.5$</td>
</tr>
</tbody>
</table>

$a$ Wetterauer (1994).

directly from the liquid phase of nitrogen. This has never been tried before.

2. Rn concentration line

In order to obtain a statistically significant activity measurement within a reasonable counting time, about 1 mBq of $^{222}\text{Rn}$ has to be accumulated from the nitrogen to be assayed. This takes into account the counting sensitivity of the proportional counter (see Section 3). At the level of 1 $\mu$Bq/m$^3$ this corresponds to a total volume of 1000 m$^3$. The allowed duration of the concentration procedure is restricted by the half-life of $^{222}\text{Rn}$ (3.8235 d). In addition fast operation is also demanded because the blank activity is increasing with time. This refers to $^{222}\text{Rn}$ that accumulates during the concentration cycle either from the decay of $^{226}\text{Ra}$ contaminations in the adsorber and in other components of the line or from Rn that leaks in from the atmosphere. As a compromise we have chosen a collection volume of 1000 m$^3$. At such conditions adsorption on charcoal at liquid nitrogen temperature ($-196^\circ\text{C}$) is the method of choice. The high adsorption coefficient of charcoal at low temperatures allows to minimise the size of the charcoal trap and thus to keep the blank activity low.

2.1. Charcoal adsorber

Charcoal is known to contain strongly variable $^{226}\text{Ra}$ concentrations that depend on the original material as e.g. coal or coconut shell. The latter is mostly much lower in Ra. Since the charcoal is the most critical contributor to the blank activity, a systematic survey was done to select low-Ra charcoal by means of low level Ge spectrometry (Heusser, 1991). From the best candidates more sensitive $^{222}\text{Rn}$ emanation measurements were performed. Some results of these measurements are listed in Table 1. The quoted uncertainties include 1$\sigma$ statistical uncertainty and uncertainties in the counting efficiencies. Upper limits are given at the 90% confidence level. There seems to exist no correlation among the four measured gamma emitting nuclides. The ‘activated carbon’ (a synthetic charcoal from Carbo Act International) has by far the lowest $^{226}\text{Ra}$ specific activity. It was only detectable by $^{222}\text{Rn}$ extraction assay from a larger sample (about 160 g). This low density charcoal was recognised to have also very favourable desorption characteristics, i.e. Rn is released easily at elevated temperature.

The adsorption coefficient of the ‘activated carbon’ for $^{222}\text{Rn}$ at $-196^\circ\text{C}$ was measured to be $(2.4 \pm 1.5) \times 10^{-7}$. Wojcik (1998) measured a consistent lower limit of $1.6 \times 10^{-7}$ with another method. In the first case a small diameter test column of that charcoal was spiked with $^{222}\text{Rn}$ and the $^{214}\text{Pb}$ activity distribution (after having reached equilibrium) was measured by gamma spectrometry. This measurement was repeated after extended flushing of the trap (cooled in a liquid nitrogen bath) with nitrogen gas. The adsorption coefficient was evaluated from the displacement of the $^{214}\text{Pb}$ activity distribution. This gas chromatographic method is well suited to investigate Rn adsorption and its spatial distribution in chromatographic columns (Bruns, 1976).

The dimensions of the charcoal column for the concentration line were adjusted to a reasonable gas velocity for adsorption and the requirement of a save enclosure of the trapped Rn, even for nitrogen samples up to 1000 m$^3$. The very low $^{226}\text{Ra}$ contamination of this charcoal allows one to slightly oversize the length
of the column without a strong increase of the blank activity. In this way possible non-uniform velocity distributions across the cross-section of the trap, which would broaden the adsorption profile of Rn are also taken into account. A diameter of 80 mm and 250 mm length (156 g activated carbon) represent a good compromise. The charcoal is enclosed between sinter plates (brass) of 80 μm pore size in a stainless steel cylinder. Three steel-enclosed Pt-100 sensors are welded into the cylindrical container at different positions of the charcoal trap for temperature monitoring. The container was electropolished inside prior to charcoal filling and joint welding in order to minimise the surface contamination. The trap has a mechanical pressure indicator and a rupture disk for protection from overpressure. Two identical traps of this kind are mounted in series in such a way that each one can be bypassed.

2.2. Line construction

The complete concentration line is designed and constructed at high vacuum standard. Only metal sealing was applied for joints and components like a particulate filter (0.003 μm particle retention) in front of the charcoal, valves (metal bellows) and pressure/vacuum indicators. Earlier tests with elastomer seal suffered from Rn released from the intrinsic Ra content of the trap. Rotation-, membrane-, and turbo-pumps as well as seal or high permeability for atmospheric Rn. Earlier tests with elastomer seal suffered from charcoal, valves (metal bellows) and pressure/vacuum indicators. The line is evacuated together with the charcoal at a rate of about 20 m3/h and a pressure of 5 mbar. The line is mounted on wheels so that it can be moved to different nitrogen ports of the Borexino experiment. It is therefore coined MOREX — movable radon extraction line.

2.3. Concentration procedure

The extraction procedure for Rn from nitrogen using MOREX includes the following steps:

- The line is evacuated together with the charcoal trap.
- The trap is baked out at ≈200°C with a slight purge of purified He applied at the end to assure complete removal of any residual Rn.
- After the trap is cooled to −196°C in a liquid nitrogen Dewar (automatically refilled from a 300-l transport tank) the nitrogen gas flows through one of the traps at a rate of about 20 m3/h and a pressure of about 2 bar. When the sample collection is complete the column is evacuated first at −196°C and then at −100°C to remove trapped nitrogen.
- Next the collected Rn is transferred from the heated charcoal column to a small cooled transportation trap (0.8 g of the same charcoal) by He purge.
- The transportation trap is dismounted and connected to the counter filling line.
- Rn is released again at high temperature, purified from inert gases by getter sorption and pushed into the proportional counter together with the counting gas (90% Ar + 10% CH4).

The blank activity of the whole procedure for measuring 500 m3 nitrogen is in the range of 20–50 μBq. This value was obtained by combining the measured individual blanks of the filter, the trap and of other parts of MOREX. The 222Rn activity of the individual blanks was accumulated for several days (close to saturation) in order to achieve acceptable measurement uncertainties. Even so, the results have large uncertainties, due to the extremely low levels of 226Ra. All three parts of MOREX contribute about equally to the 222Rn level. The combined blank is obtained from the saturation activities taking into account the time interval at which these parts are involved in the concentration procedure. Fortunately, the blank is as low that even in sub μBq/m3 measurements its correction is in the 10% range of the signal.

The recovery of Rn tested with a 222Rn spike that was added to the nitrogen stream turned out to be 100 ± 5%.

From the blank activity and the total recovery it is clear that the required sensitivity has been well achieved.

3. Proportional counting

The miniature proportional counters applied in this work (Wink et al., 1993) have a sensitive volume of about 1 cm3. They are filled with 1 bar of counting gas (90% Ar + 10% CH4). Under these conditions the alphas from the decay of 222Rn and its progenies are mostly not totally adsorbed, therefore a more continuous spectrum without pronounced spectral features is registered. Above an energy threshold of 50 keV the total counting efficiency for internal counting of 222Rn and its progenies ranges from 124 to 147%. Such efficiencies can be achieved since there are three successive alphas detectable per one 222Rn decay. The alphas of the wall deposited 218Po and 214Po have a lower detection probability than those of the homogeneously distributed 222Rn. We have two types of miniature proportional counters in use. They have different active to passive volume ratios (Wink et al., 1993) and therefore the efficiency varies in the above mentioned range.

The calibration was repeatedly measured with an extracted Rn sample from a certified 228Ra solution (PTB — Physikalisch Technische Bundesanstalt Braunschweig). Energy calibration is performed with X-rays of an external 55Fe source that shines through
a thin quartz window positioned at the end of the proportional counter.

In this counting mode the background rate of the proportional counters is in the range of one to a few counts per day, depending on the individual counter. They are shielded only by 10 cm of lead, but even without such shielding the background is increased only little. At this low background, spectral information is superfluous for further background reduction. Nevertheless, the spectrum is recorded in order to recognise malfunctions of the counter. The energy resolution of the $^{55}$Fe peak is used as an indicator for the quality of the counting gas and helps to recognise insufficient purification of the extracted Rn sample from non-inert gases, such as e.g. oxygen. The pre-treatment of the Rn-containing sample and the dominant alpha particle detection at the energy threshold of 50 keV (in such small counters) assures that only $^{222}$Rn is registered. $^{220}$Rn is too shortliving and is therefore recognised in the counting periods of several days.

The low background and the high counting efficiency make this miniature proportional counter the most sensitive detectors for $^{222}$Rn available anywhere.

4. Rn purification of liquid nitrogen

Early measurements of nitrogen gas that was directly evaporated from standard liquid nitrogen (99.999% purity including rare-gases) showed insufficient $^{222}$Rn purity by 1–2 orders of magnitude if compared to the intended level of $\mu$Bq/m$^3$ (see Table 2). Therefore, it was necessary to develop a method for Rn reduction in nitrogen.

We have considered four possibilities: (a) an improved quality liquid nitrogen supply, (b) cryoadsorption in the gas phase, (c) cryo-adsorption in the liquid phase and (d) slow evaporation of liquid nitrogen (boil off), so that the dissolved Rn remains in the liquid phase. Option (a) and (d) would be very costly and option (b) would consume excessive amounts of nitrogen due to the necessity to recool the evaporated nitrogen in the adsorption step. Hence, we have chosen option (c). Since this is a new technique, laboratory tests were required. They were performed by us and at Krakow (Wojcik, 1998) with Rn-spiked liquid nitrogen.

Based on these findings a low temperature adsorber column system, called LTA (low temperature adsorber) was designed for the production of 100 m$^3$/h gaseous nitrogen and built by the company Messer-Griesheim.

Dimensions of the adsorber column are: inner diameter 110 mm and length 1210 mm. The 11.5-l volume between stainless steel sinter plates is filled with 2 kg of ‘activated carbon’, identical to that used for the adsorption traps of MOREX. The whole column is made from electropolished stainless steel with welded joints. It is housed in a Dewar which is automatically refilled with liquid nitrogen from the same common storage tank supply. A heating mantle is fixed around the trap cylinder with temperature indicators implemented. It is used in the repurification cycle of the trap to bake out the charcoal. This cleaning procedure has to be carried out well before the adsorbed Rn reaches the end of the column and starts to recontaminate the nitrogen. For this action, the nitrogen flow has to be interrupted; the trap and the Dewar are emptied, then the trap is baked at about 200°C and is evacuated simultaneously. So far the standing time of the column has only been tested up to 7 days of full nominal flow (100 m$^3$/h). No degradation of the Rn-purity was observed.

Behind the LTA the purified liquid nitrogen is evaporated in a special electric heater and the gas then enters the general supply line of the Borexino experiment. MOREX can be hooked up to this line to assay the Rn-purity from time to time. A bypass around the LTA allows to sample unpurified liquid nitrogen to test and to control the performance of the Rn purification system.

The LTA has also a small extension line with pumps, pressure gauges, a trap, etc. for the quantitative recovery of the adsorbed Rn from the big 11-l trap. This enables an additional measurement to the assays of the unpurified and the purified nitrogen samples.

Table 2

<table>
<thead>
<tr>
<th>Nitrogen sample</th>
<th>$^{222}$Rn activity ($\mu$Bq/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase of storage tank, Heidelberg</td>
<td>$63 \pm 10; 43 \pm 6; 54 \pm 7$</td>
</tr>
<tr>
<td>Liquid phase of storage tank, Heidelberg</td>
<td>$144 \pm 16$</td>
</tr>
<tr>
<td>Purified by LTA, Heidelberg</td>
<td>$\leq 25; \leq 5$</td>
</tr>
<tr>
<td>Liquid phase of storage tanks, Gran Sasso</td>
<td>$51 \pm 8; 27 \pm 4; 78 \pm 12$</td>
</tr>
<tr>
<td>Purified by LTA, Gran Sasso</td>
<td>$0.3 \pm 0.3; 0.5 \pm 0.3; 0.7 \pm 0.1; 0.3 \pm 0.1$</td>
</tr>
</tbody>
</table>
The procedure is similar to that described for the cleaning cycle, except that the released Rn is not directly exhausted but transferred to a transportation trap of 10 g charcoal by means of a He purge.

5. Measurements and discussion

Several measurements with MOREX and the LTA have been performed at Heidelberg with a small test plant. Unfortunately, the high blank activity contribution of the used atmospheric evaporator did not allow to fully exploit the performance of the LTA. This was only possible when it was installed together with the special electric evaporator at the Gran Sasso Laboratory. Filling lines and proportional counting stations exist at Heidelberg as well as at Gran Sasso.

Some of the most important results measured at both places are given in Table 2. The quoted uncertainties include 1σ statistical uncertainty and the uncertainty of the Rn transfer from the nitrogen into the proportional counter. Upper limits are given with 90% confidence level. The transfer factor has been determined only for a total nitrogen volume of about 40 m³. Whether this can be directly applied to larger volumes needs still to be tested. Also other additional, yet unknown systematic uncertainties in this new, extremely sensitive analysis cannot be fully excluded.

If we compare the data with the given uncertainties, there seems to be some variation in the ²²²Rn content of the raw liquid nitrogen at Gran Sasso, but not so at Heidelberg. However, if averaged over the respective three measurements there is perfect agreement at about 50 μBq/m³. Possible reasons for such variation could be: (a) variation in the quality of the liquid nitrogen supply, (b) different storage times after delivery, so that a higher initial concentration decays accordingly, (c) dependence on the liquid level in the storage tanks, caused by emanation from inner wall ²²⁶Ra contaminations. If the liquid level decreases the area of the inner surface that gets warmer increases and more Rn is emanated. The available data do not allow the identification of the ²²²Rn source.

The difference between the gas phase and the liquid phase supply of the Heidelberg storage tank could reflect the purification effect of slow evaporation (boil off). However, this interpretation is rather speculative. We also would hesitate to state that the difference measured in the purified nitrogen at Gran Sasso is real.

The main aim of this investigation was to reach the sensitivity level of µBq/m³ and to find a suitable method for Rn reduction in nitrogen. That both have been achieved is well demonstrated by the data.

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References


