Measurement of the specific activity of $^{39}$Ar in natural argon

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Abstract

We report on the measurement of the specific activity of $^{39}$Ar in natural argon. The measurement was performed with a 2.3-liter two-phase (liquid and gas) argon drift chamber. The detector was developed by the WARP Collaboration as a prototype detector for WIMP Dark Matter searches with argon as a target. The detector was operated for more than two years at Laboratori Nazionali del Gran Sasso, Italy, at a depth of 3,400 m w.e. The specific activity measured for $^{39}$Ar is 1.01±0.02(stat)±0.08(syst) Bq per kg of nat Ar.

Key words: $^{39}$Ar specific activity, low-background experiments, cosmogenic activation

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1 Introduction

A 2.3-liter two-phase (liquid and gas) argon drift chamber [1] was developed and built by the WARP collaboration as a prototype detector for WIMP Dark Matter searches with argon as a target [2]. The detector was operated for more than two years by the WARP collaboration at Laboratori Nazionali del Gran Sasso, Italy, at a depth of 3,400 m w.e. One important by-product of the operation of the prototype WARP detector was the precise determination of the \(^{39}\)Ar specific activity in natural argon. \(^{39}\)Ar and \(^{85}\)Kr are two radioactive nuclides whose activity in the atmosphere is of the order of 10 mBq/m\(^3\) and 1 Bq/m\(^3\), respectively [3,4]. As a result of the liquid argon production process, they are both present in abundant quantities and are the two most significant radioactive contaminations in liquid argon. The two isotopes decay primarily by \(\beta\) emission, and their presence can limit the sensitivity of experiments looking for low energy rare events (WIMP Dark Matter interactions, neutrinoless double beta decay) using liquid argon either as a target or as a shielding material. \(^{85}\)Kr is not a pure \(\beta\) emitter, owing to the presence of a 0.43% branching ratio for decay with \(\beta\) emission on a metastable state of \(^{85}\)Rb, which then decays by emitting a \(\gamma\)-ray of energy 514 keV, with a half-life of 1.01 \(\mu\)s [5]. The coincidence between the \(\beta\) and \(\gamma\) emitted in a fraction of the \(^{85}\)Kr decays may ease in some cases the task of determining experimentally the activity of \(^{85}\)Kr in low-background detectors. The determination of the specific activity of \(^{39}\)Ar is intrinsically more challenging and not as widely discussed in the literature [3,6]. A theoretical estimate is presented in Ref. [7].

In the last twenty years liquid argon technology has acquired great relevance for astroparticle physics applications. Several experimental techniques, employing liquid argon as sensitive medium, have been proposed especially for rare events detection [2,8,9,10,11,12,13,14]. For WIMP Dark Matter direct detection, the discrimination of nuclear recoils from the \(\beta-\gamma\) induced background plays a crucial role. The discrimination provided by the experimental technique must be sufficient to reduce the radioactive background below the very low interaction rates foreseeable for WIMP Dark Matter. A precise determination of the intrinsic specific activity of \(^{39}\)Ar is therefore of significant interest for the design of WIMP Dark Matter detectors employing argon as a target.

2 The 2.3-liter WARP detector

The detector consists of a two-phase argon drift chamber with argon as a target. Two-phase argon drift chamber was first introduced within the ICARUS program [9] in the framework of a wide-range study of the properties of noble
The drift chamber (see Figure 1) is operated at the argon boiling point (86.7 K) at the atmospheric pressure of the Gran Sasso Laboratory (about 950 mbar) [15]. The cooling is provided by a thermal bath of liquid argon, contained in an open stainless steel dewar, in which the chamber is fully immersed. The pressure of the gas phase on the top of the chamber is naturally equalized to the surrounding atmospheric pressure.

Ionizing events inside the liquid argon volume produce scintillation VUV light mainly at 128 nm. The scintillation light is shifted to wavelengths in the blue by an organic wavelength shifter (TetraPhenilButadiene) covering the walls, and collected by photomultiplier tubes (PMTs) located in the gas phase and facing the liquid volume below. The 2-inch PMTs are manufactured by Electron Tubes Ltd (model D757UFLA) and have a special photocathode that ensures functionality down to liquid argon temperatures. The quantum efficiency at the emission wavelength of TPB is about 18%. The material of the PMTs has been selected for high radiopurity: according to the supplier’s specifications, the total $\gamma$ activity above 100 keV is 0.2 Bq/PMT, dominated by the $^{232}$Th and $^{238}$U chains.

A series of field-shaping rings surrounding the liquid phase superimpose an electric field of 1 kV/cm. The electrons are drifted toward the anode (located atop the chamber) and then extracted from the liquid to the gaseous phase by a local extraction field provided by a couple of grids. The electrons are linearly multiplied in the gas phase by a second, stronger local field. The PMTs detect the primary scintillation light (directly produced by the ionizing event)
and also the secondary scintillation light (produced by the electron multiplication process in the gas phase). The PMT signals are summed and sent to a multi-channel analyzer recording the pulse height spectrum. The liquid argon contained in the chamber is Argon 6.0 supplied by Rivoira S.p.A. The liquid argon is successively purified from electronegative impurities down to an equivalent contamination of less than 0.1 ppb of O$_2$ by using the chemical filter Hopkalit™ from Air Liquid. The purity from electronegative elements is actively maintained by means of continuous argon recirculation through the chemical filter.

The experimental set-up is located in the Laboratori Nazionali del Gran Sasso underground laboratory (3,400 m w.e. of rock coverage). The flux of cosmic ray muons is suppressed by a factor of $10^6$ with respect to the surface (residual flux $1.1 \mu/(m^2 \cdot h)$, average muon energy 320 GeV [16]). The detector is shielded by 10 cm of lead, to reduce the external $\gamma$ background.

The sensitive volume of the detector has the shape of frustum of cone and it is delimited by a stainless-steel cathode. The sensitive volume for the configuration under analysis is $1.86 \pm 0.07$ liter. The density of liquid argon in the operating conditions (950 mbar and 86.7 K) is $1.399 \text{ g/cm}^3$ [15]. The sensitive volume is viewed by seven PMTs, whose responses have been equalized in gain. Daily calibrations ensure the long-term stability and the linearity of the response. The sensitive volume and the argon thermal bath are contained in a stainless steel dewar, 50 cm internal diameter and 200 cm internal height.

3 Data analysis

For the measurements described in this work, the electric fields were switched off and the chamber was operated as a pure scintillation detector. The gain of the PMTs has been set up to optimize the data acquisition in the typical energy range of the environmental $\gamma$-ray background, namely up to 3 MeV. The energy threshold for data acquisition is about 40 keV. The threshold used for analysis is 100 keV, in order to exclude events from electronic noise. The response of the detector to $\gamma$ radiation was studied using different $\gamma$-ray sources ($^{57}$Co, $^{60}$Co, $^{137}$Cs) placed outside the chamber. The spectra obtained with the $^{57}$Co and $^{137}$Cs sources are shown in Figure 2. Typical values of the resolution observed with the calibration sources are $\sigma(E)/E = 13\%$ at 122 keV ($^{57}$Co) and $\sigma(E)/E = 6\%$ at 662 keV ($^{137}$Cs). The correlation between energy and primary scintillation light detected was linear within the range tested with our sources. The energy resolution of the detector can be described empirically by the following parametrization:

$$\sigma(E) = \sqrt{a_0^2 + a_1 E + (a_2 E)^2},$$ (1)
Fig. 2. Energy spectra taken with external γ-ray sources, superimposed with the corresponding Monte Carlo simulations. (a) $^{57}$Co source ($E = 122$ keV, B.R. 85.6%, and 136 keV, B.R. 10.7%), (b) $^{137}$Cs source ($E = 662$ keV).

where $a_0 = 9.5$ keV, $a_1 = 1.2$ keV and $a_2 = 0.04$. The three terms take into account the effects from non-uniform light collection ($a_2$ term), statistical fluctuations in the light production ($a_1$ term) and electronic noise ($a_0$ term).

The $\beta$-$\gamma$ spectrum in the detector (35 hours of live time) is displayed in Figure 3. The total counting rate is about 6 Hz (4.2 Hz above the analysis threshold). A simulation based on the GEANT4 toolkit [17] has been developed to reproduce and understand the observed features. The simulation takes into account the following two components of background:

- External radiation from radioactive contaminants in the materials surrounding the liquid argon volume (stainless steel, thermal bath, PMTs). Only $\gamma$-emitters are taken into account, that originate an effective $\gamma$-ray flux through the surface of the sensitive volume. This includes: $^{238}$U and daughters (especially $^{222}$Rn dissolved in the external liquid argon), $^{232}$Th and daughters, $^{60}$Co and $^{40}$K. The presence of these sources has been confirmed with a portable NaI $\gamma$-spectrometer inserted into the empty dewar.
- Bulk contaminations in the liquid argon of the chamber. In this case, both $\beta$ and $\gamma$ emitters are relevant. The most important contributions are from $^{222}$Rn, $^{39}$Ar and $^{85}$Kr.

The signal from internal $^{222}$Rn and its daughters can be monitored by counting the $\alpha$ decays of the isotopes $^{222}$Rn, $^{218}$Po and $^{214}$Po in the energy region 5–7 keV.

Other radioactive isotopes of Ar, as $^{37}$Ar and $^{41}$Ar, are short-lived ($T_{1/2}$ are 35 days and 109 min, respectively) and their cosmogenic production is negligible in the underground laboratory. The long-lived $^{42}$Ar ($T_{1/2} = 32.9$ y) is expected to be present in natural argon because of thermonuclear tests in the atmosphere; however, its concentration in $^{nat}$Ar is negligible, $< 6 \cdot 10^{-21}$ g/g (at 90% CL) [18], corresponding to less than 85 µBq/liter in liquid argon.
Table 1
Characteristics of the $\beta$ decays of $^{39}$Ar and $^{85}$Kr.

| Isotope | Half-life | $\beta$ end-point (keV) | $\beta$ mean energy (keV) |
|---------|-----------|------------------------|--------------------------|
| $^{39}$Ar | 269 y     | 565                    | 220                      |
| $^{85}$Kr | 10.8 y    | 687                    | 251                      |

MeV. After a new filling with freshly produced liquid argon the chamber shows a total $^{222}$Rn decay rate of the order of $1−2$ Hz. Due to the $^{222}$Rn half-life of 3.8 days, the observed rate decreases to few tens of events/day four weeks after the filling. Therefore, $\beta$ decays from the Rn daughters $^{214}$Pb and $^{214}$Bi can be neglected, provided the measurement is performed a few weeks after the filling of the chamber. The counting rate due to the decay of $^{14}$C (dissolved in the liquid argon or located in the surrounding plastics) is estimated to be much less than 50 mHz. Most of the $^{14}$C events occur close to the chamber walls.

The main characteristics of the $^{39}$Ar and $^{85}$Kr $\beta$ decays are summarized in Table 1. Since both decays are classified as forbidden unique $\beta$ transitions ($\Delta I \Delta \pi = 2^-$), the $\beta$ spectrum is not described by the usual Fermi function. For the present work, we assumed the $\beta$ spectra from Ref. [5].

The Geant4-based simulation is used to generate normalized spectra $s_i(E)$ from the different radioisotopes, taking into account the energy resolution of the detector. The isotopes from the natural radioactive chains are treated independently. A $\chi^2$ fit of the experimental spectrum $F(E)$ is then performed in the energy range from 100 keV to 3 MeV with a linear combination of the single components, i.e.

$$F(E) = \sum_i w_i \cdot s_i(E).$$

The coefficients $w_i$ are treated as free parameters and represent the counting rates induced by the single sources. In Figure 3 we show the experimental spectrum, superimposed with the output of the fit (i.e. $\sum w_i s_i(E)$). The fit is satisfactory in all the energy range considered. The signals from the most important external $\gamma$-rays radioactivity sources and from internal contaminations are shown in Figure 4, as derived from the analysis of the experimental spectrum.

4 Discussion

Figure 4 shows that the energy region 2−3 MeV is dominated by interactions of $\gamma$-rays from $^{232}$Th daughters, the region 1.5−2 MeV by $\gamma$-rays from $^{238}$U daughters, and the region 0.5−1.5 MeV by $\gamma$-rays from $^{60}$Co and $^{40}$K. Below
Fig. 3. Black histogram: background energy spectrum observed running the 2 liters detector deep underground at LNGS inside a 10 cm thick Pb shielding. The superimposed red histogram is the result of a fit with a Monte Carlo simulated signal (see text).

0.5 MeV the main contribution comes from $\beta$ decays from internal contaminations of $^{39}\text{Ar}$ and $^{85}\text{Kr}$; the two isotopes account for 65% of the total counting rate between 100 and 500 keV.

The cosmogenically-originated $^{39}\text{Ar}$ contamination of $^{\text{nat}}\text{Ar}$ in the troposphere was measured in Ref. [3] to be $(7.9 \pm 0.3) \cdot 10^{-16}$ g/g; the quoted error was statistical only. Since the liquid argon used for the experiment is produced from the atmospheric gas, a similar $^{39}\text{Ar}/^{\text{nat}}\text{Ar}$ ratio is expected to be present in our sample.

$^{85}\text{Kr}$ is mainly produced as fission product of uranium and plutonium. Its abundance in the atmosphere is of the order of 1 Bq/m$^3$, corresponding to about $4 \cdot 10^{-15}$ g($^{85}\text{Kr}$)/g($^{\text{nat}}\text{Ar}$) in air. Nevertheless, the distillation procedure for the production of liquid argon substantially reduces the $^{85}\text{Kr}$ fraction. The residual $^{85}\text{Kr}$ in liquid argon may vary in different batches of liquid.

In order to better show the Ar and Kr signals, Figure 5 displays the spectrum obtained from the experimental data after subtracting the fitted contribution from the other sources. The single $^{39}\text{Ar}$ and $^{85}\text{Kr}$ contributions can be disentangled from the different end-point energies, 565 keV and 687 keV respectively. Since $^{85}\text{Kr}$ and $^{39}\text{Ar}$ decays populate the same energy region of the

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3 The $^{39}\text{Ar}/^{\text{nat}}\text{Ar}$ ratio was measured for dating purposes. The knowledge of the absolute $^{39}\text{Ar}$ specific activity was hence not necessary.
The energy spectrum observed with the 2 liter detector can be reproduced by: (a) an external component dominated by interactions of γ-rays coming from U, Th, ⁶⁰Co and ⁴⁰K radioactivity of the materials surrounding the liquid argon; (b) an internal component dominated by ³⁹Ar and ⁸⁵Kr β contaminations inside the liquid argon.

The specific activity of ³⁹Ar in liquid argon resulting from the analysis is $1.41 \pm 0.02 \text{(stat)} \pm 0.11 \text{(syst)}$ Bq/liter ($1\sigma$) (see below for the discussion of systematic uncertainties). The corresponding $³⁹\text{Ar}/³⁹\text{Ar}_{\text{nat}}$ mass ratio is $(8.0 \pm 0.6) \cdot 10^{-16}$ g/g, with errors summed in quadrature. The result is in excellent agreement with the atmospheric determination of Ref. [3].

From the fit it is also obtained that the ⁸⁵Kr activity in the sample under investigation is $(0.16 \pm 0.13)$ Bq/liter ($1\sigma$). In a previous measurement performed with a sample of Argon 99.999% from Air Liquid, it was found a ⁸⁵Kr activity three times larger. This indicates that a non-negligible ⁸⁵Kr contamination may be found in commercial liquid argon samples. In this case, an additional fractional distillation could be required to reduce the radioactive background for the WARP experiment.

The systematic uncertainties are summarized in Table 2. The dominating item is related to the energy calibration of the detector response: since the discrimination between ³⁹Ar and ⁸⁵Kr is based upon the β end-points, the fit result is sensitive to the energy calibration and resolution. The uncertainty on the energy calibration in the range of interest was evaluated to be 2% ($1\sigma$) from the measurements with the γ-ray sources; the corresponding ³⁹Ar systematic error is 6.5%. The second important contribution is related to the uncertainty in the active volume of the chamber. The filling level can be determined with accuracy of about 1 mm, and the diameter of the teflon container with the
Fig. 5. Residual energy spectrum observed in the WARP chamber after subtraction of the expected contribution from external $\gamma$-rays. The spectrum is well described by a combination (dashed line) of $\beta$ decays of $^{39}\text{Ar}$ and $^{85}\text{Kr}$.

Table 2
Systematic uncertainties on the $^{39}\text{Ar}$ specific activity.

| Item               | Relative error | Absolute error (Bq/liter) |
|--------------------|----------------|---------------------------|
| Energy calibration | ±6.5%          | ±0.092                    |
| Energy resolution  | ±1.3%          | ±0.018                    |
| Sensitive mass     | ±3.8%          | ±0.054                    |
| Total              |                | ±0.11                     |

reflector fixed on it is known with a precision of about 2 mm. This corresponds to an uncertainty on the sensitive mass of 3.8%.

5 Conclusions

The best estimate of the $^{39}\text{Ar}$ specific activity in the liquid argon is $(1.41 \pm 0.11)$ Bq/liter, or $(1.01 \pm 0.08)$ Bq/kg of natural Ar, or $(8.0 \pm 0.6) \cdot 10^{-16}$ g($^{39}\text{Ar}$)/g($^{\text{nat}}\text{Ar}$). The value is consistent with the previous determination by H. Loosli [3]. The uncertainty in our measurement is mainly due to systematics.

The liquid argon sample under investigation shows a contamination of $^{85}\text{Kr}$,
Fig. 6. Confidence regions (1σ, 2σ and 3σ) for the $^{39}$Ar and $^{85}$Kr specific activities. Systematic uncertainties have been added in quadrature.

0.16±0.13 Bq/liter (1σ).

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