Effects of Nitrogen contamination in liquid Argon

R. Acciarri, a M. Antonello, a,b B. Baibussinov, c M. Baldo-Ceolin, d P. Benetti, e F. Calaprice, f E. Calligarich, g M. Cambiaghi, f N. Canci, a F. Carbonara, h F. Cavanna, a,l S. Centro, d A.G. Cocco, i F. Di Pompeo, a,b G. Fiorillo, b C. Galbiati, j V. Gallo, l L. Grandi, a,b G. Meng, i I. Modena, a C. Montanari, g O. Palamara, h L. Pandola, b G.B. Piano Mortari, a F. Pietropaolo, i G.L. Raselli, g M. Roncadelli, g M. Rossella, a C. Rubbia, b E. Segreto, b,l A.M. Szelc, j,a S. Ventura c and C. Vignoli g

aUniversità dell’Aquila e INFN, L’Aquila, Italy
bINFN - Laboratori Nazionali del Gran Sasso, Assergi, Italy
cINFN - Sezione di Padova, Padova, Italy
dUniversità di Padova e INFN, Padova, Italy
eUniversità di Pavia e INFN, Pavia, Italy
fPrinceton University - Princeton, New Jersey, U.S.A.
gINFN - Sezione di Pavia, Pavia, Italy
hUniversità di Napoli e INFN, Napoli, Italy
iINFN - Sezione di Napoli, Napoli, Italy
jIFJ PAN, Krakow, Poland

E-mail: ettore.segreto@lngs.infn.it, flavio.cavanna@aquila.infn.it

ABSTRACT: A dedicated test of the effects of Nitrogen contamination in liquid Argon has been performed at the INFN-Gran Sasso Laboratory (LNGS, Italy) within the WAirP R&D program.

A detector has been designed and assembled for this specific task and connected to a system for the injection of controlled amounts of gaseous Nitrogen into the liquid Argon. The purpose of the test is to detect the reduction of the Ar scintillation light emission as a function of the amount of the Nitrogen contaminant injected in the Argon volume. A wide concentration range, spanning from $\sim 10^{-1}$ ppm up to $\sim 10^3$ ppm, has been explored.

Measurements have been done with electrons in the energy range of minimum ionizing particles ($\gamma$-conversion from radioactive sources). Source spectra at different Nitrogen contaminations are analyzed, showing sensitive reduction of the scintillation yield at increasing concentrations.

Direct PMT signal acquisition exploiting high time resolution by fast waveform recording allowed high precision extraction of the main characteristics of the scintillation light emission in contaminated LAr. In particular, the decreasing behavior in lifetime and relative amplitude of the

1Corresponding author
slow component is found to be appreciable starting from $\mathcal{O}(1 \text{ ppm})$ of Nitrogen concentrations. The rate constant of the quenching process induced by Nitrogen in liquid Ar has been found to be $k_Q(N_2) = 0.11 \pm 0.01 \, \mu s^{-1} \text{ppm}^{-1}$, consistent with a previous measurement of this quantity but with significant improvement in precision. On the other hand, no evidence for absorption by $N_2$ impurities has been found up to the higher concentrations here explored.

**KEYWORDS**: Scintillators, scintillation and light emission processes (solid, gas and liquid scintillators); Noble-liquid detectors (scintillation, ionization two-phase); Instrument optimisation

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1 Introduction

The search for Dark Matter in the form of WIMPs is of primary interest in the present astroparticle physics scenario. Direct detection of Dark Matter with liquified noble gases as target media is one of the most promising lines of development in experimental technology. The two-phase (liquid-gas) technology developed and first operated by the WArP Collaboration [1] is based on the simultaneous detection of both signals produced by ionization events in liquid Argon (LAr): free electron charge and scintillation light.

In the case of the ionization charge, its full collection is limited mainly by the electron attachment process due to contaminations of electro-negative impurities like Oxygen present at residual level in (commercial) Argon. Detailed studies by the Icarus Collaboration [2] led to the development of adequate purification systems (Oxygen reactants and molecular sieves, down to $\leq 0.1$ ppb of Oxygen equivalent concentration), normally employed in experimental applications.

On the other hand, the effects of impurities on the scintillation light yield are less precisely explored.

Quenching (i.e. non-radiative) processes in two-body collisions of impurity-molecules with Ar$^*_2$ excimer states (otherwise radiatively decaying with scintillation light emission) and Absorption of the emitted VUV photons by photo-sensitive impurities may take place depending on the type of
impurity and its concentration level. This led to include within the WArP R&D program investigations on Oxygen and Nitrogen contamination effects on LAr scintillation light. Two experimental tests have been thus performed.

The case of Nitrogen (N$_2$), present in commercial Argon at the level of 1 to 10 ppm, depending on the selection grade, is the subject of the present study (while results from the test with Oxygen are reported separately [3]).

The quenching effect in N$_2$-contaminated LAr has been observed, affecting in particular the slow component of the scintillation emission. This effect is relevant not only because it imposes some limitations on the full collection of the light available, but also because it deteriorates the detector capability of Pulse Shape discrimination of background events (electrons from $\gamma$ interactions) from the signal (Ar-recoils, potentially induced by WIMP interactions) [1].

On the other hand, no evidence for photo-absorption has been detected, as a priori expected from the very low Nitrogen photo-absorption cross section in the VUV range of the LAr scintillation emission.

2 Features of the scintillation radiation in LAr

It is experimentally established and theoretically well understood that recombination and de-excitation processes following the passage of ionizing particles in liquid Argon (LAr) finally originate scintillation radiation [4, 5]. In particular, interactions of ionizing particles in LAr cause the formation of both electron-hole(Ar$^+$) pairs and Ar$^*$ excited atoms (the ratio Ar$^*$/Ar$^+$ of the numbers of excitons and ion pairs produced being 0.21 [6]). Ar$^*$ excited atoms lead to the formation of the Ar$^*$ low excited dimer through collision with Ar atoms (“self-trapping” process, [7]). On the other hand, Ar$^+$ ions also lead to the formation of Ar$^*_2$ through a number of subsequent processes including electron recombination [7]. The excited dimer states formed in both cases in LAr are recognized to be the singlet $^1\Sigma_u$ and the triplet $^3\Sigma_u$ excimer states in the M-band that characterize the solid Argon structure [8]. The rise-time corresponding to excimer formation and relaxation is very fast for both components: $\mathcal{O}$(1-10 ps) from self-trapping [9] and $\mathcal{O}$(100 ps) from recombination [7].

The de-excitation processes to the dissociative ground state $^1\Sigma_g$ lead to scintillation light emission in the Vacuum Ultra-Violet (VUV) region:

$$\text{Ar}_2^* \rightarrow 2 \text{Ar} + 1 \gamma$$ (2.1)

In liquid phase, various electron-to-ion recombination mechanisms along the ionization track are active, depending on the type of the ionizing particle and on its LET (Linear Energy Transfer, i.e. the specific energy loss along the path) [6]. These mechanisms affect the number of excited dimers Ar$^*_2$ produced per unit of deposited energy, as well as the relative populations of the singlet and triplet states. For a mip the photon yield has been measured to be $4.0 \times 10^4 \gamma$/MeV [6].

The $\gamma$ decay wavelength spectrum of both excimer states has been extensively investigated. It is well represented by a gaussian shape, peaking at $\lambda \simeq 128$ nm with $FWHM \simeq 6$ nm (at boiling point $T=87.3$ K, $\rho = 1.395$ g/cm$^3$) [10]. The time dependence of the photon emission from Ar in liquid phase is known less precisely. The various measured values of both the excimer lifetimes and of the relative amplitudes reported in literature are in fact quite different with each other. To a first approximation, in all measurements the overall scintillation light emission exhibits a double
exponential decay form, characterized by two very different components: a fast component, with a time constant $\tau_S$ in the 2 ns to 6 ns range, and a slow component, with a time constant $\tau_T$ in the 1100 ns to 1600 ns range. These are associated to the lifetimes of the singlet $^1\Sigma_u$ and of the triplet $^3\Sigma_u$ states in LAr, respectively (see [10] for a compilation of available lifetime data from past experiments and [11, 12] for more recent results).

In addition to these fast and slow components, a less intense intermediate component (with decay time around 40 ns) has been also sometime reported in literature [13, 14], the origin of which was never investigated in details nor definitively confirmed.

While the time constants do not depend appreciably on the ionization density, the amplitude ratio $A_S/A_T$ of the singlet and triplet states is found to be strongly affected by this quantity [15]. In particular, all measurements show an enhancement of the $^1\Sigma_u$ formation (fast component) at higher deposited energy density.\footnote{This effect is contrary to the effect in organic scintillators, in which the relative intensity of the slow component increases with increasing specific ionization density.}

As an example, the relative amplitude for the fast and for the slow component in case of a mip is reported to be $A_S/A_T = 0.3$ [13] (i.e. $A_S = 23\%$ and $A_T = 77\%$ respectively), while for heavily ionizing particles the intensity ratio increases (e.g. $A_S/A_T = 1.3$ for $\alpha$-particles and $=3$ for nuclear recoils, but higher values are given elsewhere [16]). This wide separation is an important feature of the scintillation signals in LAr, leading to define robust Pulse Shape Discrimination criteria suitable for particle identification.

The lack of accuracy/consistency in the presently available lifetimes data can presumably be ascribed to (i) light quenching from residual (unknown) concentration of impurities diluted in LAr, (ii) limited time resolution employed in past experiments, (iii) dependence on the LAr density (not systematically reported or accounted for).

### 2.1 Quenching and photo-absorption from diluted N$_2$ impurities in LAr

The de-excitation rate can be described by a first-order rate law, characterized by the two decay time constants $\tau_S$ and $\tau_T$ associated to the singlet $^1\Sigma_u$ and the triplet $^3\Sigma_u$ excimer states of Ar$^*_2$, respectively ($j = S, T$):

$$
\frac{d [\text{Ar}^*_2]^j}{dt} = - \frac{1}{\tau_j} [\text{Ar}^*_2]^j \Rightarrow [\text{Ar}^*_2]^j(t) = [\text{Ar}^*_2]^j(0) e^{-t/\tau_j}
$$

Assuming that one scintillation photon per Ar$^*_2$ dissociation is produced, the time dependence of the scintillation light emission in pure LAr can thus be represented by the following probability distribution function (pdf):

$$
\ell(t) = \frac{A_S}{\tau_S} \exp \left( -\frac{t}{\tau_S} \right) + \frac{A_T}{\tau_T} \exp \left( -\frac{t}{\tau_T} \right)
$$

with the sum of the relative amplitudes constrained to unity ($A_S + A_T = 1$) so that

$$
\int_0^\infty \ell(t) dt = (A_S + A_T) = 1.
$$

\footnote{The same time dependence (eq. (2.3)) applies for Ar in gas phase, though with substantially different triplet component lifetime (e.g. $\tau_T \approx 3200$ ns) [17]. In (pure) liquid Argon the shorter lifetime is sometime assumed to be due to "medium effects" becoming relevant in Ar condensed states [10].}
Residual concentration at the ppm (part per million) level of N$_2$, O$_2$, H$_2$O and CO+CO$_2$ contaminants (whose presence is usually indicated in commercially available Argon) can lead to a substantial reduction of the scintillation light intensity due to both the quenching process acting on the excited Ar molecular states before de-excitation photon emission and the absorption process of the emitted scintillation photons. In principle, other processes may also take place, involving the excited atomic states (Ar*) before excimer formation, as excitation transfer and (non radiative) quenching to/by impurity molecules. However, these reactions, seen in Ar gas mixtures, have negligible influence in liquid Argon (as discussed below).

Argon purification systems (Oxygen reactants and molecular sieves) are known to be very effective in reducing the O$_2$ and H$_2$O, CO+CO$_2$ contamination up to a negligible level ($\leq 0.1$ ppb, part per billion). At present, methods for removing the N$_2$ residual content in Argon are instead less commonly used in experimental applications, and the effects of N$_2$ contamination are rather poorly known.

The Nitrogen photo-absorption process has been extensively investigated in aeronomy and the absorption cross section measured in a wide range of photon wavelengths [19] (room temperature, low pressure). In the VUV range ($10 \leq \lambda \leq 200$ nm) the cross section is large, $\sigma(10$ Mb), only at the short wavelengths ($\leq 100$ nm), while in the higher range (of the LAr scintillation emission) the absorption drops by several orders of magnitudes, $4 (< 10^{-3}$ Mb) [19].

In pressurized gases photo-absorption tends to be higher due to cross section broadening from pressure effects. In liquid solution at cryogenic temperatures (as for N$_2$ in LAr) a similar effect is also expected, though difficult to be quantitatively defined. The N$_2$ absorption coefficient $k_A$ averaged over the LAr wavelength spectrum ($\lambda_{peak} = 128$ nm) (i.e. the probability of Ar scintillation photo-absorption by Nitrogen molecules diluted at a given concentration in LAr) has been estimated. Even accounting for a possible large broadening due to density effects (gaussian spread $\sigma_G < 8$ nm), its value remains very low, $k_A < 0.0001$ ppm$^{-1}$cm$^{-1}$. Assuming this value as an upper limit, Nitrogen absorption is relevant only in presence of macroscopic contaminations (above the permil level) and/or for very large LAr volume detectors (photon mean free path of the order of tens of metres, for Nitrogen concentrations in the ppm range). In the present study the effect of photo-absorption by Nitrogen is therefore considered negligible up to the higher contaminations here explored. The validity of this assumption has been probed and verified as reported in section 5.

Quenching of excited atomic states (Ar*) by N$_2$ molecules can take place, in competition with exciton "self-trapping" leading to Ar$_2^*$ formation. The total cross section for the quenching of atomic Ar$^*$ states by N$_2$ is known ($\sigma_{Q}^{At} = 580$ Mb) [20]. The main contribution (about one-half of the total quenching cross-section [21]) is due to excitation transfer to N$_2$ excited molecular states (emitting the UV band at 337 nm in Ar gas mixtures, under suitable pressure conditions). In liquid Argon (T=87 K) mixtures the total N$_2$ quenching cross section corresponds to a rate constant$^6$ of

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$^3$O$_2$ and CO+CO$_2$ are known to be electro-negative molecules. Their high $e$-affinity induces ionization electron attachment, with dramatic effects on detectors based on charge collection (LAr-TPC). N$_2$ molecules are not electro-negative [18], and therefore no appreciable effects on the free electron charge can be expected.

$^4$The Lyman-Birge-Hopfield bands and other forbidden transitions are present at wavelengths between 145 and 100 nm, but the maximum cross sections measured are less than $10^{-3}$ Mb (e.g.: H Ly $\alpha \cdot 122$ nm, $\sigma_A \leq 6 \times 10^{-3}$ Mb) [19].

$^5$The absorption coefficient is defined as $k_A(\lambda) = \frac{\sigma_A(\lambda) n(N_2)}{A}$, where $\sigma_A$ is the Nitrogen absorption cross section (in cm$^2$) at wavelength $\lambda$, $n(N_2)$ the density per ppm of contaminant in LAr in units of ppm$^{-1}$ cm$^{-3}$.

$^6$The rate constant is defined as $k_Q = \sigma_Q^{At}(\nu)$, where $\langle \nu \rangle$ is the Boltzman average relative velocity. For N$_2$ in liquid Ar (T=87 K) $\langle \nu \rangle \approx 10^5$cm/s [14].
\[ \approx 5.8 \times 10^{-12} \text{cm}^3 \text{s}^{-1}, \text{equivalent to 0.12 ppm}^{-1} \mu \text{s}^{-1}. \] At a given concentration \([N_2]\) (e.g. in ppm units) the quenching time \((1/k_Q[N_2])\) can be calculated \((\approx 8 \times 10^{-6} \text{s at 1 ppm})\). Excitons self-trapping in LAr is a much faster process \((6 \times 10^{-12} \text{s}, [9])\). Therefore, excimer formation in LAr is not appreciably depleted by exciton quenching up to the extreme \(N_2\) concentrations.

The relevant reaction to be considered is thus the quenching process in two-body collision of \(N_2\) impurities with \(Ar^*_2\) excimer states [14]:

\[
Ar^*_2 + N_2 \rightarrow 2Ar + N_2
\]

This non-radiative collisional reaction\(^7\) is in competition with the de-excitation process leading to VUV light emission. As a result, the population of the “photon precursors” \((Ar^*_2)\) is depleted before light emission and a sensitive reduction of the scintillation light yield is eventually expected.

In more details, the quenching process leads to the decrease of the excimer concentration \([Ar^*_2]\), while the contaminant concentration \([N_2]\) stays constant in time. Therefore, to a first approximation, also for this case a first-order rate law can be assumed and characterized by the \(Ar^*_2\) quenching rate constant \(k_Q(N_2)\):

\[
\frac{d[Ar^*_2]}{dt} = - k_Q [N_2] [Ar^*_2] \Rightarrow [Ar^*_2](t) = [Ar^*_2](0) e^{-k_Q[N_2]t},
\]

From an early study reported in literature [14] (1982)\(^8\) the value of this rate constant is \(k_Q \simeq 3.8 \times 10^{-12} \text{cm}^3 \text{s}^{-1}\) (equivalent to \(\simeq 0.1 \text{ ppm}^{-1} \mu \text{s}^{-1}\)). This value indicates that quenching is a rather slow process, nonetheless effective already at modest concentrations in reducing (mainly) the long-lived (triplet) component of the excimer concentration.

The time dependence of the scintillation light emission in \(N_2\)-contaminated LAr can be represented by an expression formally identical to eq. (2.3):

\[
\ell'(t) = \frac{A'_S}{\tau'_S} \exp\left(-\frac{t}{\tau'_S}\right) + \frac{A'_T}{\tau'_T} \exp\left(-\frac{t}{\tau'_T}\right)
\]

where \(\tau'_j [j = S, T]\), the effective (decreased) lifetime of each component, is a function of the \([N_2]\) concentration:

\[
\frac{1}{\tau'_j([N_2])} = \frac{1}{\tau_j} + k_Q [N_2]
\]

and \(A'_j\), the effective (quenched) amplitude, is also function of the \([N_2]\) concentration:

\[
A'_j([N_2]) = \frac{A_j}{1 + \tau_j k_Q [N_2]}
\]

Notice that under these definitions \(\ell'(t)\) reduces exactly to \(\ell(t)\) for \([N_2]=0\), namely for pure Argon. The sum of the quenched amplitudes of eq. (2.7) is no longer constrained to unity:

\[
\int_0^\infty \ell'(t) dt = (A'_S + A'_T) \leq 1
\]

\(^7\)Excitation transfer from \(Ar^*_2\) levels to \(N_2^*\) states is unlikely, owing to energetic considerations [21]. Therefore, \(N_2\) quenching of \(Ar^*_2\) excimers is purely non-radiative.

\(^8\)In this study [14] the scintillation properties of Nitrogen-doped liquid (and solid) Argon have been studied and compared to Argon-Nitrogen gas mixtures. A decrease in the decay time of the LAr triplet component has been observed at increasing \(N_2\) concentration and attributed to \(Ar^*_2\) quenching. On the other hand, emission of UV photons from Nitrogen excimers, as found in Argon-Nitrogen gas mixtures, was not detected in \(N_2\)-doped liquid Argon.
From eq. (2.10) the *Surviving Fraction* with respect to quenching can be defined and hereafter indicated as $Q_F$:

$$Q_F = A'_S + A'_T \quad ; \quad 0 \leq Q_F \leq 1$$

(2.11)

namely, the ratio between the total intensity of scintillation light emitted for a given $[N_2]$ contamination with respect to the case of pure liquid Argon. $Q_F$ also represents, by definition, the normalization value for $\ell'_j(t)$ under the present assumption of negligible photo-absorption.

This work is dedicated to a systematic study of the effects of Nitrogen contamination in LAr. In particular, the aim is:

- to determine the fraction $Q_F$ of the $Ar^*_2$ excimers, produced at the stage of primary energy deposition in LAr, surviving to quenching process by $N_2$ contamination [section 4];
- to determine the effective lifetimes $\tau'_j$ as a function of the $N_2$ contamination for each component, as well as the quenched amplitudes $A'_j$ [section 5];
- to extract the main characteristics of the scintillation light emission in pure LAr and the value of the rate constant $k_Q(N_2)$ of the quenching process associated to the presence of $N_2$ contaminant [section 5.1].

### 3 Detector and experimental method

A detector has been designed and assembled at the INFN-LNGS external facility (“Hall di Montaggio”) for this specific task. It consists of a cylindrical LAr cell in PTFE (h=12 cm, $\varnothing$=8.5 cm internal dimensions, wall thickness 0.5 cm) containing about 0.7 lt of LAr (about 1 kg of active mass), viewed by a single 2” photo-multiplier (Electron Tubes ETL D745UA) mounted on the top end of the cell.

The photo-multiplier (PMT) is manufactured to work at cryogenic temperatures (LAr); however, the glass window is not transparent to the 128 nm LAr scintillation light. Therefore, the PMT optical window is coated with a thin plastic film (polystyrene matrix) of TetraPhenyl-Butadiene (TPB), an efficient frequency down-converter with emission spectrum peaked at 430 nm and width of about 50 nm (FWHM) [22], well matching the PMT sensitivity range.

To enhance the light collection, a TPB coated reflector layer surrounds the internal walls (side and bottom) of the PTFE cell. The reflector substrate (VM2000 by 3M) is a dielectric, multi-layer polymeric mirror (99% specular reflectivity). The TPB deposition was obtained by spraying a volatile solution (toluene solvent) containing a defined fraction of diluted TPB.

The detector is housed in a stainless steel cylindrical vessel (h=85 cm, $\varnothing$=10 cm), closed at both ends by vacuum-tight ConFlat (CF100) flanges, figure 1 (schematic layout). The internal volume of the chamber is about 6.5 lt and it contains, after filling, a total amount of 3.0 lt of LAr, including the LAr cell active volume at its bottom. The LAr active volume of the detector cell inside the chamber is made optically independent but not partitioned from the rest of the volume, to allow even distribution of the $N_2$ solute. The vessel is immersed in a LAr bath of a stainless steel open dewar, to liquify and keep the LAr internal volume at stable temperature.

A transfer line for the Ar filling and for the injection of controlled amounts of gaseous Nitrogen (GN$_2$) has been also assembled and connected to the LAr chamber via vacuum-tight
Figure 1. Schematic layout of the experimental set-up for the N₂ contamination test.

Table 1. Argon 6.0 (from Rivoira Supplier) purity specifications: maximum impurity levels.

| Impurity          | Maximum Impurity Level |
|-------------------|------------------------|
| Oxygen (O₂)       | ≤ 0.2 ppm              |
| Nitrogen (N₂)     | ≤ 0.5 ppm              |
| Water (H₂O)       | 0.5 ppm                |
| Hydrogen (H₂)     | 0.1 ppm                |
| Total Hydrocarbons (THC) | 0.05 ppm          |
| Carbon Dioxide (CO₂) | 0.05 ppm              |
| Carbon Monoxide (CO) | 0.05 ppm              |

pipes and feed-throughs. The line includes a two-stage system formed by a gaseous Nitrogen (GN₂) buffer and a mixer of gaseous Nitrogen and Argon, connected via UHV valves, figure 1. The internal volume of the buffer is precisely known and accurate pressure control allows the injection of controlled amounts of N₂ gas in the LAr volume (from 1 ppm to 300 ppm of N₂ per injection with ≤ 6% precision).

Gaseous Argon (GAr) for filling, supplied by a 200 atm pressurized bottle, is the best grade 6.0 (99.9999%) commercial Argon, with impurity concentration below 1 ppm. In table 1 the purity specification for the GAr in use is reported [23].

The GAr from the 6.0-bottle is flushed during filling through a Hydrosorb/Oxisorb cartridge
positioned along the GAr line for partial removal\textsuperscript{9} of O\textsubscript{2} and H\textsubscript{2}O. The GN\textsubscript{2} for the controlled contamination is 5.5 GN\textsubscript{2} type (99.9995\%), also supplied by a pressurized bottle.

In figure 2 a picture taken during the test is shown.

After vacuum pumping of the whole system (detector chamber and transfer line) up to a residual vacuum of few 10\textsuperscript{-5} mbar, the external bath is filled with commercial LAr, the GAr line is opened and the purified Ar gas feeding the detector chamber is liquified inside it up to reaching a given level, precisely monitored by a level meter, corresponding to 3.0 ±1.5\% lt of LAr.

At LAr working conditions of T=86.5 K, P=930 mbar (\(\rho_{\text{Ar}}=1.40\) g/cm\textsuperscript{3}), contamination with GN\textsubscript{2} is performed by a controlled procedure: (1) GN\textsubscript{2} corresponding to a given fraction of the LAr molar quantity\textsuperscript{10} in the chamber is first transferred into the GN\textsubscript{2} buffer volume (at controlled temperature and pressure), (2) the valve to the GN\textsubscript{2}+GAr mixer is opened, (3) GN\textsubscript{2} is injected into the chamber by repeated flushes of purified GAr through the mixer, (4) data taking starts after few hours of delay from the N\textsubscript{2} contamination.

Ar and N\textsubscript{2} form almost ideal vapor/liquid mixtures. In the liquid phase they are completely miscible. The dilution process is rather slow, however the speed is substantially increased by the repeated flushing of GN\textsubscript{2}+GAr mixture through the liquid. In the top part of the chamber (about 3.5 lt of gas above the liquid level), the vapor pressure is different for Argon and Nitrogen.

\textsuperscript{9}No recirculation system is implemented for further O\textsubscript{2} purification. Initial content of residual N\textsubscript{2} in the 6.0 Ar is not filtered out. Additional contaminations from material out-gassing inside the chamber cannot be excluded.

\textsuperscript{10}The concentration units in use here are ppm, parts per million (atomic, often indicated as ppma). This indicates the ratio between the number of interesting elements (in our case N\textsubscript{2} molecules) to ordinary elements (Ar atoms).
Figure 3. PMT Electronics read-out chain.

and can be determined by the Antoine equation assuming the gas at the same temperature of the liquid Ar. Nitrogen results to be more volatile than Argon by a factor of 3; therefore the Nitrogen concentration in gas phase is higher than in the liquid [24]. However, since the gas/liquid volume ratio for Ar is very large (e.g. 835 at STP), the fraction of the N\textsubscript{2} injected in the chamber which is diluted in the LAr volume is very close to one.

3.1 Data taking

The PMT read-out system is structured as an oscilloscope channel: in fact, the PMT+read-out chain can be represented by the simplified scheme of figure 3, where at the first stage the PMT signal is duplicated by a linear Fan-out, one output being used as input for a Constant Fraction Discriminator (CFD) providing a trigger signal when a defined threshold is passed, and the second output is directly recorded by a fast Waveform Recorder (Acqiris, DP235 Dual-Channel PCI Digitizer Card). At each trigger from the CFD the signal waveform is recorded with sampling time of 1 ns over a full record length of 10 \(\mu\)s. A LabView application has been developed for the data acquisition and storage. In figure 4 a typical waveform recorded during the N\textsubscript{2} test is shown.

After the filling procedure with purified 6.0 Argon was completed, the N\textsubscript{2} experimental test started on February 2007 and lasted about one month. The test was performed by adding progressively controlled amounts of N\textsubscript{2} and exposing the LAr cell to \(\gamma\)-sources after each contamination. Data samples (\(\gtrsim 10^5\) waveforms per run, trigger rate \(\sim 0.5\) kHz) have been recorded in two independent runs per N\textsubscript{2} contamination, with \(^{137}\text{Cs}\) and \(^{60}\text{Co}\) \(\gamma\)-ray sources.

After the first run at "0 ppm" (i.e. no additional N\textsubscript{2} injection to the initial purified 6.0 Argon), the contamination levels were set to the values reported in table 2.

The initial amount of Nitrogen in LAr at filling stage is indeed unknown (though constrained to \(\leq 0.5\) ppm, according to 6.0 Ar specifications of table 1). Its actual value represents an offset ([N\textsubscript{2}\text{in}]) to be determined (section 5.1) and added to the contamination value to obtain the absolute N\textsubscript{2} concentration: [N\textsubscript{2}]+[N\textsubscript{2}\text{in}] \(\rightarrow\) [N\textsubscript{2}\text{Abs}].
Figure 4. Typical (single) waveform recorded during the N$_2$ test. Event with large energy deposition from cosmic muon (mip) crossing the LAr cell.

Table 2. [N$_2$] Contamination level injected in the LAr cell during the tests.

| N$_2$ Contamination [ppm] | Nominal   |
|---------------------------|-----------|
| 0.97 ± 0.06               | 1 ppm     |
| 1.93 ± 0.08               | 2 ppm     |
| 6.62 ± 0.15               | 7 ppm     |
| 11.45 ± 0.19              | 12 ppm    |
| 21.12 ± 0.27              | 20 ppm    |
| 40.45 ± 0.39              | 40 ppm    |
| 59.77 ± 0.48              | 60 ppm    |
| 98.43 ± 0.62              | 100 ppm   |
| 494 ± 14                  | 500 ppm   |
| 988 ± 21                  | 1000 ppm  |
| 2966 ± 40                 | 3000 ppm  |

Single photo-electron measurements were also acquired before and after each $\gamma$-source run, to provide calibration data (see appendix A) useful at various stages of the analysis performed.

4 Signal amplitude analysis

Gamma rays from the $^{60}$Co source (1.27 and 1.33 MeV) induce mainly single Compton interactions in the LAr cell active volume (Compton edge $E_C \simeq 1$ MeV), with final state electron in the mip
range. Scintillation light is emitted and, after down-conversion and reflections at the active volume boundaries, is collected at the PMT photo-cathode; finally the signal waveform is recorded.

By single waveform off-line integration, the absolute (individual) signal amplitude is obtained in units of photo-electrons$^{11}$ (proportional to the electron energy deposited in the LAr cell).

Pulse amplitude spectra have been thus obtained for each run at different $[N_2]$ value with the $^{60}$Co source, as reported in figure 5 [Left]. Manifestly, the spectra are progressively down-scaled (i.e. the light yield (phel/MeV) reduces) at increasing $N_2$ concentration.

As discussed in section 2.1, this effect is entirely attributed to $N_2$ quenching [reaction (2.5)] of a fraction of the $Ar_2^*$ excimers, mainly those in Triplet state, since the absorption of the emitted photons (from the $Ar_2^*$ fraction surviving quenching) is expected to be negligible, due to the very low $N_2$ photo-absorption cross section in the VUV range.

Therefore, the scale factor from uncontaminated to $N_2$ contaminated spectra (i.e. the ratio of the light yield at a given $N_2$ contamination to the yield of pure liquid Argon) corresponds to $Q_F$, the previously defined $Ar_2^*$ Surviving Fraction with respect to quenching (eq. (2.11)).

A dedicated fitting procedure has been developed to determine the $Q_F$ value from the corresponding $N_2$ contamination run data: each individual entry value of the uncontaminated (0 ppm) spectrum is down-scaled by a factor $Q_F$ ($0 \leq Q_F \leq 1$) and randomly fluctuated with a gaussian spread $\sigma_Q$ around the down-scaled value assumed as its mean value to take into account worsening of the detector resolution due to lower light yield. A down-scaled “trial spectrum” is thus obtained, depending on $Q_F$ and $\sigma_Q$ free parameters of a $\chi^2$ minimization procedure to best fit the trial spectrum to the experimental one ($[N_2]$ contaminated). As an example, in figure 5 [Right]

$^{11}$The absolute signal amplitude is calculated by integration of the single recorded waveform over the whole length of the recorded time window (10 $\mu$s), after baseline determination and subtraction, and converted into photo-electron units by using the calibration constant from single photoelectron response.
the result from the fitting procedure for the [N$_2$]=20 ppm run is reported ($Q_F$([20 ppm])=0.405: i.e. only ∼40% of Ar$_2^*$ survive quenching and emit a photon, while the remaining ∼60% undergo non-radiative N$_2$ collisions).

The $Q_F$ values and associated errors obtained from the analysis of the whole set of $^{60}$Co runs at the various N$_2$ contaminations are given in figure 6. The first point ("0 ppm additional contamination" of the first run after 6.0 Ar filling) is set to $Q_F = 1$ for relative normalization.

The errors on the plot are from the fit (statistical) and are appreciable at the highest concentrations. After a fast drop up to ∼100 ppm ($Q_F([100 ppm])=0.25$) a slower decrease is observed at higher N$_2$ concentrations (notice the log-log scale in use). The light contribution from the long-lived Triplet component is in fact expected to vanish above [N$_2$] ≥ 100 ppm, and the fast Singlet component starts to be progressively affected by the quenching process because of the very high Nitrogen concentration.

The fit values of the gaussian parameter $\sigma_Q$ increase as expected with the contamination level (from few to few tens of phel). These correspond to the variation of the detector resolution due to the decreased light yield at increasing N$_2$ contaminations.

5 Signal shape analysis

As reported in section 3, data were collected by full signal waveform recording (1 ns sampling time over a time window of 10 $\mu$s) for each trigger event. This allows a detailed reconstruction of the signal shape, in particular of the individual components (relative amplitude and decay time) of the scintillation light following an ionization event in LAr.
To this purpose the recorded waveforms (wfm) have been appropriately treated\(^\text{12}\) and averaged (\(\overline{V}(t)\)) for each \([N_2]\) run, \(\approx 10^5\) events) and the averaged waveform amplitude (area) normalized to the corresponding \(Q_F\) value.

The averaged signal can be symbolically expressed as:

\[
\overline{V}(t) = S(t) \otimes \mathcal{R}(t)
\]

where \(\mathcal{R}(t)\) is the \textit{Response Function} of the read-out system (PMT+cable+wfm digitizer), i.e. the electronic \textit{impulse response} defined by the output signal obtained from an input single photo-electron pulse (usually indicated as SER, Single Electron Response).

The true light signal shape \(S(t)\) is then obtained from the recorded waveform \(\overline{V}(t)\) by a standard deconvolution procedure [25], using the SER function \(\mathcal{R}(t)\) experimentally obtained, as explained in appendix A. As examples, three averaged signals \(S(t)\) (at \([N_2]=0\) ppm, 12 ppm and 40 ppm) after SER deconvolution are shown in figure 7.

The signal function \(\ell'(t)\) (see eq. (2.7)) convoluted with a gaussian function has been used to fit the signal shape \(S(t)\) from each \([N_2]\) run. The gaussian spread (free parameter \(\sigma_G \approx 4\) ns from fit) takes into account the time resolution of the light collection at the detector sensitive area, due to transit time of the PMT, wavelength shifting time, time spread due light propagation including multiple reflections at the volume boundaries, etc.

Attempts to perform a fit with a signal function characterized by two time components (singlet and triplet) failed, as evident from figure 8. This led to use a three components model \((S, T\) and \(I)\).

---

\(^{12}\)Individual waveforms (wfm) are off-line processed: (1) noisy and saturated events are first removed, (2) 0.5 \(\mu\)s of baseline presamples are used for individual baseline determination and subtraction, (3) energy cuts on wfm amplitude (integral) are applied, from the Compton spectrum with \(600\) keV \(\leq E \leq 1100\) keV, (4) wfm are time equalized at the same peak position and finally (5) selected wfm’s are summed together.
Figure 8. Signal shape at 0 ppm contamination (black histogram) with comparison of two-components (red line) vs. three-component (blue line) model.

Intermediate), nicely fitting the present data (color lines in figure 7). The presence of an intermediate component is thus confirmed, in agreement with some earlier indications [13]. Whether this has a physical origin or is an instrumental artifact is not clear. Dedicated studies on the origin of it are under way. Based on preliminary considerations, reported in appendix B, light emission from Nitrogen in LAr is unlikely, while yet unknown intrinsic physical properties of Argon or uncontrolled instrumental effects appear as possible contributions to this component.

Both amplitudes and decay times, as determined from the fitting procedure of the signal shapes at different N\textsubscript{2} concentrations, show no correlation with the energy cuts (wfm selection with 600 keV ≤ E ≤ 1100 keV) applied to obtain the averaged signals.

The decay times τ\textsuperscript{′}j of the individual components from the fit as function of N\textsubscript{2} contamination are reported in figure 10.

The quenched amplitudes of the individual components A\textsuperscript{′}j from the fit are shown in figure 9. The total amplitude (sum of the A\textsuperscript{′}j amplitudes at given [N\textsubscript{2}], black stars in figure 9) is constrained (eq. (2.11)) to the corresponding Q\textsubscript{F} value previously obtained (figure 6). This is due to the average waveform normalization adopted here (eq. (2.11)), under the present assumption of negligible photo-absorption.

As cross-check of this assumption, the sum of the relative amplitudes at [N\textsubscript{2}] over the sum of the relative amplitudes at [N\textsubscript{2}]=0 ppm (uncontaminated run) has been evaluated. By definition this ratio gives the fraction of the excimer states surviving quenching. Its value should coincide with the Q\textsubscript{F} value if, besides quenching, no other mechanisms leading to further LY loss are active. No difference (within error) has been found between the values of these two quantities\textsuperscript{13} at each [N\textsubscript{2}]...
Figure 9. Effective amplitudes (mip electronic recoil) of the individual components ($A'_j, j = S, T, I$ in different color and symbol) as function of the absolute N$_2$ concentration ([N$_2$]$_{Abs} = [N_2] + [N_2]_{Im}$). The total amplitude (sum of the $A'_j$ amplitudes at given [N$_2$]) is constrained to the corresponding $Q_F$ value (black stars) obtained in section 4. Full lines in corresponding color are from the fit with saturation model (eq. (5.3)), while dotted lines refer to the fit without saturation hypothesis (eq. (2.9)).

Figure 10. Effective decay times of the individual components ($\tau'_j, j = S, T, I$ in different color and symbol) as function of absolute N$_2$ concentration. For [N$_2$] $\geq$ 500 ppm, $\tau'_T \rightarrow 0$ (not shown). Full lines in corresponding color are from the fit with saturation model (eq. (5.2)), while dotted lines refer to the fit without saturation hypothesis (eq. (2.8)).
Table 3. Results from the overall fit: characteristics of scintillation radiation in LAr from mip electronic recoil and of quenching process from Nitrogen contamination. Quoted errors are statistical from the fit (saturation model).

| Lifetimes | Amplitudes | N\textsubscript{2} quenching rate constant | Initial N\textsubscript{2} concentration |
|-----------|------------|-------------------------------------------|----------------------------------------|
| $\tau_S = 4.9 \pm 0.2$ ns | $A_S = 18.8\%$ | $k_Q = 0.11 \pm 0.01 \text{ ppm}^{-1} \text{ s}^{-1}$ | $[\text{N}_2]\text{in} = 0.40 \pm 0.20 \text{ ppm}$ |
| $\tau_I = 34 \pm 3$ ns | $A_I = 7.4\%$ | | |
| $\tau_T = 1260 \pm 10$ ns | $A_T = 73.8\%$ | | |

point. Therefore this comparison confirms the validity of the assumption made here (based on N\textsubscript{2} absorption cross-section data, section 2.1).

5.1 Characteristics of LAr scintillation light and of N\textsubscript{2} quenching process

The quenched amplitudes and the decreased lifetimes of the scintillation light in N\textsubscript{2}-contaminated LAr are correlated variables depending on the intrinsic LAr scintillation characteristics and on the rate constant of the N\textsubscript{2} quenching process, as reported in section 2.1.

An overall fit of the data obtained from the signal shape analysis reported in figure 9 and figure 10 has been performed using eq. (2.9) and eq. (2.8) as fitting functions, respectively. The values of eight free parameters have been thus obtained by $\chi^2$-minimization: the LAr scintillation characteristics (intrinsic lifetimes $\tau_j$ and relative amplitudes $A_j$, $j = S, T, I$ for mip electronic recoils), the rate constant $k_Q$ of the quenching process due to N\textsubscript{2} contaminant, and the initial Nitrogen concentration $[\text{N}_2]\text{in}$. This last corresponds to the N\textsubscript{2} content in the 6.0 grade Argon used for the initial filling. Its value is obtained by using an additive free parameter in the fitting functions: $[\text{N}_2]\rightarrow[\text{N}_2]+[\text{N}_2]\text{in}$.

A contamination of Oxygen at the level of $[\text{O}_2]=0.06$ ppm has been taken into account into the fit, as determined by the analysis reported in [3] from the parallel test of Oxygen contamination effects.

The curves, (dotted lines in corresponding color) in figure 9 and figure 10, show the result of the fit. The values of the parameters obtained from the fit are reported in table 3.

The rate constant ($k_Q$ value) of the quenching of Ar\textsuperscript{2} excimers\textsuperscript{14} by N\textsubscript{2} impurities is in agreement with the earlier measurement found in literature [14].

The initial N\textsubscript{2} concentration (relative to the “0 ppm additional contamination” run) is within the expected range from the specifications of the 6.0 grade Ar used for filling.

The relative amplitude of the intermediate component is small ($A_I = 7.4\%$) compared to the amplitude of the other two components. It is also worth noticing that the amplitude ratio between $A_S + A_I$ and $A_T$ is 0.35 in agreement with available reference data for light ionizing particles [13].

In all scintillation light components the fit (dotted lines) is found to deviate from the data at the highest N\textsubscript{2} concentrations, as possibly due to incomplete dilution of impurities into the liquid:

\textsuperscript{14}The rate constant of the two-body (N\textsubscript{2}-Ar\textsuperscript{2}) process is assumed to be the same for both the singlet $^1\Sigma_u^+$ and the triplet $^3\Sigma_u$ Ar excimer states. A fit has been tried with two rate constants as free parameters. This indicates that in case of N\textsubscript{2}-1\Sigma_u coupling, a slightly higher constant rate is preferred.
above ≈ 500 ppm a steeper slope from the fit is in fact expected compared to experimental data in both relative amplitudes and lifetimes.

This trend might be explained by an (apparent) saturation at increasing concentrations of the N\textsubscript{2} solute in LAr solvent. Similar indications have been reported by other groups [14] and also in our test with O\textsubscript{2} contamination [3]. All measurements were performed on relatively short time scale (about one day per contamination): at the highest contaminations the delay between N\textsubscript{2} injection and data recording was presumably not sufficient to reach the chemical equilibrium (dilution process completed). This prevents to draw any definite conclusion on long term effects at these contamination levels.

Under this saturation hypothesis a different parameterization, depending on the N\textsubscript{2} concentration, has been thus used for the fitting function of the lifetimes (each component, all available [N\textsubscript{2}] points):

\[
\frac{1}{\tau'_j} = \frac{1}{\tau_j} + k_Q \beta \left(1 - e^{-\frac{[N_2]}{\tau_j}}\right)
\]

(5.2)

and of the amplitudes:

\[
A'_j = \frac{A_j}{1 + \tau_j k_Q \beta \left(1 - e^{-\frac{[N_2]}{\tau_j}}\right)}
\]

(5.3)

where the new fit parameter \(\beta\) represents the concentration scale where saturation becomes effective (\(\beta = 530\) ppm from fit), i.e. where adding more solute does not accordingly increase the concentration of the solution and its effects. At first order approximation both formulas reduce to the original fitting functions (eq. (2.8) and eq. (2.9)).

The curves in figure 9 and figure 10 (full line in corresponding color) show the result of the fit with the modified parameterization (saturation model - nine fit parameters including \(\beta\)).

Compared to the previous fit, this model (saturation hypothesis) improves the scaling at the highest N\textsubscript{2} concentrations and decreases the overall \(\chi^2\) (C.L. ≃ 80%). The results of the fit (\(A_j\), \(\tau_j\) and quenching rate constant \(k_Q\)) are instead practically unchanged, and the values reported in table 3 are confirmed.

The errors associated to the results in table 3 are statistical from the new fit (saturation model). These take into account the statistical errors from the fit of the signal shapes at different N\textsubscript{2} contaminations (section 5) and also the error associated to the injected amounts of Nitrogen in the contamination procedure (table 2).

Systematic uncertainty may come from different sources: instability of the signal read-out system, bias due to residual concentration of unknown types of impurities in LAr leading to further Ar-excimer quenching (this hypothesis cannot be excluded, without mass spectrometry of the impurity content of the initial LAr sample in use during the test), uncertainty introduced by the procedures of data analysis. Only this last issue has been investigated in some details.

The off-line analysis is based on the deconvolution procedure of the SER function (technical details in appendix A) to determine the light signal shapes (at the different N\textsubscript{2} contaminations) from the averaged PMT waveforms. Systematics associated to this procedure have been evaluated. In particular, for the intrinsic lifetime \(\tau_T\) the systematic uncertainty \((syst_D)\) from the propagation of the deconvolution procedure error has been estimated to be around 4%, therefore:

\[
\tau_T = 1260 \pm 10\ (stat) \pm 55\ (syst_D)\ ns
\]
This result, though compatible with several other measurements performed in past experiments, is only marginally compatible with the recent measurement reported in [11].

An additional dedicated analysis of our data has been thus performed through the development and comparison of alternative off-line procedures, including the method reported in [11] (fit of the averaged waveform). All details can be found in appendix C.

As a conclusion of this study, the discrepancy can be ascribed to the different strategies adopted in the analysis of the LAr scintillation signals. The method undertaken here, based on the SER de-convolution, looks appropriate for the treatment of our data due to its capability of mitigating instrumental effects (PMT and read-out chain), though at the expenses of a more complicated procedure.

6 Conclusions

New generation detectors based on LAr as active medium for Dark Matter direct search and for neutrino physics exploit both scintillation light and free electron charge from ionization events.

Residual content of electro-negative impurities in LAr (like Oxygen molecules) significantly reduces the amount of charge and light by attachment and quenching/photo-absorption processes respectively. This led to the development of dedicated O\textsubscript{2} purification systems, routinely employed in the experimental set-up’s.

On the other hand, non electro-negative contaminants like Nitrogen can also be found at appre- ciable concentration levels even in best grade commercial Argon. Contamination at ppm level of N\textsubscript{2} may lead to a reduction of the scintillation light intensity, due to the quenching process in two-body collision of N\textsubscript{2} impurities with Ar\textsubscript{2}\textsuperscript{\ast} excimer states otherwise decaying with VUV light emission.

No appreciable effects from N\textsubscript{2} contamination on the free electron charge can instead be ex- pected, due to the low electron affinity of the N\textsubscript{2} molecule, nor on the emitted scintillation light by photo-absorption, due to the very low N\textsubscript{2} absorption cross section in the VUV range.

A dedicated test of excimer quenching has been performed by means of a controlled N\textsubscript{2} contamina- tion procedure. Measurements have been done by \textit{mip} particle excitation (Compton electrons from \gamma-sources in the MeV range).

The effect on the scintillation light collection has been measured over a wide range of N\textsubscript{2} concentration, spanning from $\sim 10^{-1}$ ppm up to $\sim 10^3$ ppm, though a \textit{saturation} effect of the solute (Nitrogen) in the LAr solvent has been presumably found at the highest contaminations.

The Surviving Fraction $Q_F$ of the Ar\textsubscript{2}\textsuperscript{\ast} excimers, from primary energy deposition in LAr, to quenching process by N\textsubscript{2} impurities has been determined over the whole explored range of N\textsubscript{2} concentrations. The rate constant of the light quenching process induced by Nitrogen in LAr has been thus found to be $k_Q(N_2) = 0.11 \ \mu s^{-1} ppm^{-1}$ (in agreement with some early measurements reported in literature). This implies that, for example, at $\sim 1$ ppm level a $\sim 20\%$ reduction of the scintillation light is experienced due to the N\textsubscript{2} quenching process.

The experimental test also allowed to extract the main characteristics of the scintillation light emission in pure LAr, thanks to the direct PMT signal acquisition by the fast Waveform Recorder in use with the implemented DAQ system.

The light signal shape is well represented by the superposition of three components with exponential decay. The fast and the slow components, with decay time constants $\tau_5=4.9$ ns and $\tau_7=1260$ ns, are recognized to be associated to the decay of the singlet $1\Sigma_u$ and the triplet $3\Sigma_u$
excimer states of Ar$_2^*$. A less intense intermediate component ($\tau_I=34$ ns) is also found to be present (as sometime reported in literature), whose origin could presumably be in part ascribed to PMT instrumental effects.

The main effect of residual N$_2$ in LAr is of reducing the slow component lifetime at increasing concentration. This is relevant not only because it imposes some limitations on the full collection of the light potentially available but also because the ratio fast to slow of the relative amplitudes varies to higher values. All this makes the slow signals from $\gamma/e$ background less distinguishable in Pulse Shape vs the fast Ar-recoils signals possibly induced by WIMP interactions, in Dark Matter search experiments.

Therefore, the implementation of dedicated methods for removal of the residual N$_2$ content results to be recommended with LAr based detectors, or at least the use of best grade commercial Argon with reduced Nitrogen contamination (below $\sim 0.5$ ppm) appears as definitively necessary.

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A Single electron response

Single photo-electron pulses (SER data) from thermionic dark counts have been routinely acquired during the test, before and after each source run at the different N$_2$ concentrations.

Pulse amplitude spectra from SER waveform integration were used for calibration purposes. Typical SER spectrum of the PMT in use is reported in figure 11: the Gaussian distribution at higher ADC values corresponds to the genuine single photo-electron mean amplitude and spread. The mean value (gaussian fit) gives the calibration constant, from ADC units into photoelectrons units, useful for Compton spectra analysis (section 4) and checking of the detector stability in time.

The single photo-electron pulses collected by full signal waveform recording (1 Gsample/s over 10 $\mu$s time window) were used for the determination of the read-out electronics Response Function: the impulse response $R(t)$ is obtained by processing and averaging the SER waveforms with amplitude in a defined interval around the mean value of the corresponding single photo-electron pulse amplitude spectrum.

A typical SER waveform averaged on a large sample of recorded signals is shown in figure 12. This is characterized by two main features: (1) the genuine single photo-electron shape from the PMT with FWHM $\approx 10$ ns and a decay tail extending up to about 150 ns, and underneath (2) a
Figure 11. SER spectrum of the PMT in use and fit superimposed. The interval around the mean value for single photo-electron waveform selection is also indicated.

Figure 12. Example of SER averaged waveform $\mathcal{R}(t)$.

very long, slowly decreasing component up to $\sim 3\mu$s (visible in the up-right, log scale panel of figure 12) followed by a flat baseline.

The flat baseline is due to pile-up (in the average wfm) from the PMT dark counts randomly distributed in the recorded time window, while the origin of the long-decay component is not fully understood. It may be ascribed to additional pile-up of after-pulses from ionization of residual gases in the PMT (normally reported in PMT test reports [26]). Typically, these type of after-
pulses are delayed in a $O(0.5 - 5) \mu$s interval after the main signal from which they originate, in the ratio of $\leq 5\%$ to the number of true pulses.

The SER function $R(t)$ (including the pile-up components) determined for each source run is used in the deconvolution procedure to obtain the corresponding true light signal shape $S(t)$ (section 5).

The deconvolution of the response function $R(t)$ from the experimental waveform $V(t)$ is performed numerically in the frequency domain. The discrete Fourier transforms $\tilde{v}_i$ and $\tilde{r}_i$ of $V_i(t)$ and $R_i(t)$ respectively are first evaluated by the Fast Fourier Transform (FFT) algorithm [25]. According to the convolution theorem, the true light signal $S_i(t)$ is hence obtained by taking (with the same FFT algorithm) the inverse Fourier transform of $\tilde{s}_i(= \tilde{v}_i/\tilde{r}_i)$.

B The intermediate component: preliminary considerations

As described in section 5, evidence for an intermediate component in the scintillation signal shape has been found at all the N$_2$ contaminations, including the “0 ppm run” with lifetime $\tau_I \simeq 34$ ns and relative amplitude $A_I \simeq 7.4\%$. The origin of this component is controversial: it could be ascribed to (1) instrumental effects (in the PMT), (2) physical (unknown) properties of Argon, (3) presence of residual N$_2$ concentration in LAr.

Explanations in terms of:

- Light emission from Nitrogen trace in LAr, though possible, is unlikely in the present experimental conditions (this is evident by noting that no increasing $A_I$ amplitude is found at increasing N$_2$ concentrations in Ar-N$_2$ studies - [this paper] and [14]). In fact, scintillation emission from excited Nitrogen molecular states N$_2^+$ (C$^3\Pi_u$) formed by energy transfer interaction with Ar$^*$ atoms (mainly Ar($^3P_2$)), as seen in gaseous Ar-N$_2$ mixtures, is negligible since in liquid phase the precursor Ar$^*$ atoms are quickly self-trapped, leading to Ar$^*_2$ formation. However, a series of mechanisms leading to the formation of excited Nitrogen atomic states from Ar$^*_2$ energy transfer has been recently identified and detected in Ar-N$_2$(few %) gas mixtures [21]. The N$^+$ radiative decay (149 nm and 174 nm) may thus populate the intermediate component amplitude. The size of this effect, presumably small in liquid mixtures with low N$_2$ concentrations, as in the present study, is of interest for further studies.

- Intrinsic physical properties of Argon yet unknown or only marginally investigated cannot be excluded. For example, from the delayed decay of vibrationally hot Ar$^*_2$ molecules surviving vibrational relaxation [8]. This decay, seen in gas at low pressure, was never investigated in liquid phase.

- Instrumental effects to explain (at least part of) the onset of the Intermediate component is our preferred option. Such effects could be ascribed to the use of PMT and enhanced by particular experimental conditions. For example, the so called anode glow in the PMT [26] can be considered: it has long been known that electrons in PMTs induce light emission in

---

15As reported in section 2.1, the Ar$^*$ self-trapping reaction rate is $\approx 10^{11}$ s$^{-1}$ [9], while the collision frequency of the excitation transfer process can be estimated (from [21]) as $\approx 0.3 \times 10^6$ s$^{-1}$ at [N$_2$]=0.5 ppm (e.g. like in our “0 ppm run”).
the last cascades of dynode systems. Photons may take the way back to the photo-cathode and so give rise to after-pulses, typically 20 to 50 ns after the true pulse from which they originate (and up to 120 ns in large PMTs). This effect has been well characterized in various studies, indicating that the total amount is of the order of 1%.

All these are preliminary considerations. Only dedicated studies (outside the limits of this report) may possibly indicate the true origin of this component.

C Systematic error in the slow component lifetime determination

In the exhaustive paper on Scintillation time dependence and pulse shape discrimination from Lippincott et al. [11] a value for the slow component lifetime of $\tau_T=(1463 \pm 5_{\text{stat}} \pm 50_{\text{syst}})$ ns is quoted. This value is only marginally compatible with the one we found here of $\tau_T = (1260\pm 10_{\text{stat}}\pm 55_{\text{syst}})$ ns.

We ascribe this discrepancy to the different strategies adopted in the analysis of the LAr scintillation waveforms and not to physical or instrumental effects. In fact, by applying the procedure described in [11] to fit the tail of the average waveform $\mathcal{V}(t)$ obtained from the “0 ppm run” data sample we find a $\tau_T$ value for pure LAr in full agreement with the one reported in [11].

In more details, the value of the slow component lifetime we obtain with the fit model from [11] (characterized by an additional flat baseline component)

$$\mathcal{V}(t) = A \exp(-t/\tau_T) + B$$

(C.1)

is $\tau_T=(1306 \pm 5)$ ns. Taking into account that the Argon we used to fill the cell (“0 ppm run”) had indeed some residual contamination of Nitrogen and Oxygen (400 ppb of N$_2$ and 60 ppb
of $O_2$) and having determined the values of the quenching rate constants $k_Q$ for $N_2$ [this report] and $k_Q$ for $O_2$ [3] respectively, we can extrapolate the $\tau_T$ value for pure LAr, that results to be $\tau_T = (1453 \pm 10)$ ns.

In figure 13 we show the average waveform $\bar{V}(t)$ with the fit (C.1) superimposed. For comparison the light signal shape $S(t)$ as obtained from $\bar{V}(t)$ with our standard procedure based on the SER function $\tilde{S}(t)$ deconvolution is also shown. The difference in the slope of the long-component is quite evident. In our data this is due to the presence of an “extra-long tail” exponentially decaying with lifetime of $\sim 3$ $\mu$s (rather than the simple flat baseline component), also present in the SER waveform (figure 12). This possibly may fake a longer triplet state decay time in the average non-deconvoluted waveform. Thanks to the deconvolution procedure this component is washed out.

It is worth noting that when alternatively a fit of $\bar{V}(t)$ with an extra-long decay component is performed ($B \to B \exp(-t/\tau_B)$ in eq. (C.1), with $\tau_B \approx 3$ $\mu$s) the triplet component lifetime is determined within 2% spread around the value obtained from our standard procedure (SER deconvolution).

To further explore possible sources of systematic uncertainty due to the off-line procedures in our data analysis, we also tested the classic method of Coincidence Single Photo-electron Counting [27] for another determination of the long component lifetime.

The Coincidence Single Photo-electron Counting technique has been largely exploited in many reports on scintillation lifetime measurements (for LAr see [13, 14, 16]). Data recorded with our set-up (one single PMT with direct signal acquisition by fast Waveform Recorder) allow to perform an artificial single photo-electron counting experiment, based on off-line data treatment. Starting at 0.5 $\mu$s after the onset of a triggered signal, a single photo-electron identifying algorithm was run through the recorded waveform $V(t)$ and for each photo-electron pulse (defined by appropriate cuts) found at time $t_i$ a single bin with the value of 1 was substituted. As an example with the “0
ppm run” data sample, the resulting histogram, which is per se cleaned from noise contributions, provides a $\tau_T$ determination that is in very good agreement (within $\sim 2\%$) with the result of our standard procedure based on the SER function deconvolution, as shown in figure 14.

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