Study of Liquid Argon Dopants for LHC Hadron Calorimetry.

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ABSTRACT: Hadron calorimetry based on the Liquid Argon Ionisation Chamber technique is one of the choice techniques for LHC-experimentation. We propose to study in a systematic way the effect of dopants to LAr to improve on driftspeed ("Fast Liquid Argon") and on its response to densely ionising particles ("Compensated Liquid Argon"). We describe the measurements and monitoring of the critical parameters, including the use of IR absorption spectroscopy.

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1. INTRODUCTION.

Precision hadron calorimetry will be an essential detection technique for LHC experiments [1]. Very few viable calorimetry techniques have been identified, of which the LAr ionisation chamber method is widely regarded as a key contender.

The work by many groups during the past decade has led to a good understanding of the fundamental physics constraints determining the energy resolution and to a better appreciation of the relative advantages and disadvantages of competing calorimetry techniques [2]. The LAr-technique is usually credited with very good control of systematic effects. On the other hand, the drift time [3] and incomplete compensation [4] will provide a limit to the application of this technique at the LHC. Estimates indicate [3,5,6] that calorimetry based on pure LAr may be viable up to LHC luminosities $\mathcal{L} \lesssim 10^{34}$ cm$^{-2}$s$^{-1}$.

We propose a systematic study of the effects of selected dopants on LAr with the aim to achieve an improvement of both points mentioned earlier:

i) search and study of dopants to increase the drift velocity. It has been known from a long time [7] and recently confirmed in a large calorimeter [4] that CH$_4$ added at a fraction of a percent will increase the drift velocity by a factor two or more;

ii) search and study of dopants to increase the response to densely ionising particles, resulting in improved compensation. We plan to study photosensitive dopants (e.g. allene), which absorb the scintillation light produced simultaneously with the ionisation charge and which do not show any saturation as a function of ionisation density.

There is also a large interest to perform at a proper time similar studies with LXe instead of LAr. Due to its higher density, LXe is of course much more adequate for smaller-scale experiments than the ones using LAr. LXe is effectively proposed in the development of high-resolution space-born telescopes for
gamma-ray astrophysics, double beta-decay experiments and study of giant-resonances. There is no doubt that the studies performed with LAr and LXe are to some extent complementary [8].

In Section 2 we discuss in detail this dopant programme. This domain has not been intensely studied to date and its impact on calorimetry performance is mostly unknown.

Monitoring of the different parameters involved in the understanding of the response of a calorimeter is obviously essential. In case of pure liquid argon monitoring of the charge yield is sufficient. In case of doped liquid argon however, the charge yield and the drift velocity should be monitored as both vary with the level of dopant concentration.

A test set-up is described in Section 3, which will allow to measure the relevant parameters such as collected charge, drift velocity, lifetime of the liquid. For that $\alpha$ and $\beta$ sources as well as photoproduction of electrons by an UV Laser [9] are proposed. This set-up will allow us to conduct in an integrated manner the necessary studies of the different dopants and to define their optimal concentrations. Such a quantitative and systematic study has not been done yet. At the same time, it will guide us to design the probably reduced-size monitoring system to be used in situ in a full-size calorimeter without compromising the number of parameters monitored. Such precise measurements in situ will have to guarantee the essential issue of keeping systematic errors below an acceptable level.

We feel it is primordial before any construction of a future calorimeter to assert all these questions of systematics and controls in presence of high concentration of dopants. It has also to be realized that using doped liquid argon will certainly have further implications as one would abandon some of the advantages associated with the use of a pure noble gas. This is a main concern. In particular such test set-up will be convenient to study all aspects of the purification, introduction and mixing of the dopants with LAr, as well as the homogeneity and stability of the mixture. Once the correct concentration has been determined, special attention should be given in the study of the radiation damage of the dopants [10].
Related to the dopant question is the one of the impurities [8]. Electronegative impurities will ultimately be responsible for the degradation of the lifetime of the liquid, i.e. for an unexplained decrease of the collected charge and apparent mobility. Published data show such an effect, either with addition of methane or with an increase of allene concentration for example. It is currently believed that unknown dissolved impurities are responsible for such degradation of the expected performances.

Our programme also addresses the identification and monitoring of impurities. We propose to analyse impurities in the liquid phase using infrared (IR) spectrography [11,12]. Dopants and impurities have absorption spectra in the infrared region (from say 2 - 20 μ), as observed in the gas phase [13], and their concentration can then be detected by measuring the absorption of a known collimated infrared beam passing through the liquid. Section 4 describes the possibility of using such an analysis to monitor the impurities and to control the concentration of dopants (methane-like or photosensitive).

Section 5 summarizes the goals of the proposed programme.

Appendix A details general budget and manpower considerations. The contribution to the Collaboration from the Manne Siegbahn Institute of Physics, Stockholm, is described both in terms of existing facilities made available and foreseen requests. The Appendix also details the budget and manpower requested from CERN in order to set-up this entirely new apparatus on the CERN site. In addition we recommend the purchase of an IR spectrograph as a general CERN facility, in collaboration with and under the responsibility of the MT division.

Appendix B lists the milestones of the project. This R&D project has to be carried out on a fast timescale, such that the feasibility of a doped liquid argon calorimeter for a LHC experiment can be evaluated in a timely manner.

Appendix C shows the sharing of the responsibilities among the participating Institutes.
Although this proposal addresses questions related to liquid argon, many of the results are expected to be also applicable to liquid krypton, or xenon.

2. SPEED AND CHARGE COLLECTION.

As mentioned earlier, an increased drift velocity by at least a factor \( \geq 2 \) above the saturated pure liquid argon drift velocity is desirable for LHC calorimeters. For a given shaping time, shorter drift time will lead to an effective increase in the collected charge and to a reduction in the effective width of the bipolar response as can be seen in Fig. 1 [6]. Then from these considerations, one concludes that reduction of the drift time by a factor two will result in a considerable increase of the data taking rate.

Two different kinds of additives will be studied:

- doping the liquid argon with a compound known for its high drift velocity such as an hydrocarbon, e.g. methane, or TMS;
- doping the liquid argon with a photosensitive substance allowing to collect additional charge from the conversion of the UV light emitted by the liquid argon. Such photosensitive dopants at high concentration are known to increase the drift velocity, but comprehensive measurements do not exist.

Both solutions have never been systematically investigated neither in terms of optimal concentrations of additive nor in terms of unknown dissolved impurities coming along with the dopant itself. Difficulties and expectations are discussed in the next paragraphs.

2.1 Addition of methane to pure liquid argon.

Addition of a small concentration (on the order of few tenths of a percent)
of hydrocarbons leads to an increase of the drift velocity by a factor 2 at least above the saturation value of the pure liquid argon [7], see Fig.2. Two results have been also achieved successfully in large size calorimeters by adding around 0.1-0.3% of methane [4,14]. However, a reduction of the free electron yield was observed at the same time, as well as a higher value for the Birk’s constant [15], leading to an undesirable increased dE/dx saturation. The methane also absorbs all UV photons emitted by the liquid argon.

As a consequence, as shown in Figs 3a and 3b, a degradation of the energy resolution and an increase of the e/π ratio above pure liquid argon was observed by the HELIOS collaboration in a test run at the end of 1989, in which 0.3 % of methane was added to the liquid argon. In this test however, the methane was not purified but used as delivered from the manufacturer. The influence of possible impurities is not known.

Systematic studies of the optimum quantity and purity of hydrocarbon additives (such as methane or ethylene for example) remains to be undertaken and will be part of our tests.

Methane like most hydrocarbon liquids shows a high dE/dx saturation, which is the major drawback of this additive. In contrast, one expects a much smaller Birk’s constant for photosensitive dopants as explained later. This class of dopants is therefore expected to favorize an e/π ratio close to unity due to an increased signal from the densely-ionising shower components.

2.2 UV scintillation of liquid argon.

Ultraviolet luminescence from liquid argon has been studied extensively [16]. It was shown that for liquid argon 67% of the luminescence is due to excited molecules which are produced through the recombination of molecular ions and free electrons and that 33% is due to the desexcitation of self-trapped excitons by UV emission. The recombination process is field dependant whereas luminescence coming from excitons is independant of electric field.
The self-trapped exciton luminescence in liquid argon has two components, a fast one having a decay time of 5 ns and a slow one with a much larger decay time of 1.15 μs, coming from the decay of a singlet and a triplet exciton states whose lifetimes are very different (see Fig.4). It is clear that high rate operation using liquid argon luminescence (through the addition of photosensitive dopants) requires the slow component to be quenched.

Such a quenching can be achieved by adding for example either 100 ppm of liquid xenon or approximately 1% of N\textsubscript{2} [16,17]. In the case of Xe-doping of liquid argon, the quenching of the excited argon emission is attributed to the ionisation of Xe by the Ar-excitons and energy transfer to the Xe-excitons by a long range dipole-dipole mechanism. As a result the emitted UV light has the wavelength of the Xe emission, namely 175 nm instead of the 130 nm of the Ar emission. The decay spectrum is very similar to the one from the Xe-excitons (namely like Xe-emission at high electric fields), showing a decay time of 65 ns only (see Fig.5a). A similar effect can be expected by adding liquid krypton instead of xenon.

Quenching of LAr luminescence by N\textsubscript{2} (see Fig.5b) can be explained by the transfer of the Ar-excitons energy to the nearest N\textsubscript{2} atoms [17]. In that case, no UV light is emitted as the relaxation process of the N\textsubscript{2} atoms is non-radiative. A decrease in scintillation intensity is then expected with doping. The slow decay component of the luminescence is observed to be killed by the process.

The same mechanism should be present in case of photosensitive dopants. Lower concentrations are probably adequate as allene, TMS or TMA have many more vibrational excitation states. It will be easier for the Ar-excitons to interact with them. However no quantitative information on the level of quenching of the slow component is available and we will have to investigate this question.
2.3 Addition of photosensitive dopants to liquid argon.

Several photosensitive dopants have been successfully tried in very small concentrations, at the 10 - 200 ppm level [ cf Table I from Refs 18,19]. Nonpolar materials have to be chosen to avoid forming colloids and freezing out at low temperatures. The value of the vapour pressure of these nonpolar solvants are rarely available for liquid argon temperatures, but extrapolation via the Clausius-Clapeyron equation indicates very low vapor pressures. Concentrations of these dopants are extremely dependent on the temperature and a difference of few degrees can correspond to doubling the amount of photosensitive material in solution, requiring accurate monitoring. One of the most promising dopants is allene, also called propadiene, CH2=C=CH2, having an estimated pressure of around 10^-5 Torr at 90 °K [20]. All the other ones, such as TMS,TMG,TMA,TEA, have an estimated pressure below 10^-6 Torr at this temperature.

The increase in charge collection obtained with a variety of dopants is shown in Fig. 6a [18]. Fig. 6b shows the same for different concentrations of allene and TMG ( tetramethylgermanium ). These measurements have been obtained with α particles generating a strong local ionization and consequently an important recombination. The effects of the photosensitive dopants are therefore particularly enhanced relative to the increase of charge collection expected for minimum ionizing particles. This is found out by the modest increase in charge collection due to TMG in case of β particles [ Fig.6b ].

We are interested in studying more quantitatively the effects of such dopants in liquid argon, at concentrations which will also increase the drift velocity. As an example, TMS has one of the highest known drift velocity, close to methane and should act the same way, as should allene, TMG and others. One of the main goals of this project is to find the optimal concentration of the dopant, giving the maximal collected charge for a certain integration time. A technique then to control the maximum observed charge certainly calls for precise monitoring of the variations in the dopant concentration, for example in case of temperature changes.
Addition of large amounts of dopant raises several questions. As seen from Fig.7 [19] the collected charge saturates for concentration of allene above 80 ppm. Several reasons may be suspected:

- electronegative impurities brought along with the dopant;
- formation of an aggregate, the solubility of the allene in such concentrations being not sufficient;
- local inhomogeneous concentration of allene;

Two directions for R&D using dopants are particularly promising:

- allene doped liquid argon
- TMA doped liquid argon / liquid xenon (150 ppm) mixture.

### 2.3.1 Allene doped liquid argon.

The main advantages in using allene come from its high vapor pressure compared to other photosensitive dopants and its excellent quantum efficiency for photoionization in liquid argon (see Table II, from ref. [21]).

In addition allene, C₃H₄, is a relatively simple 3-dimensional molecule so its behaviour under heavy radiation is expected to be favorable.

Allene is delivered by industry under gas form with a N₂O purity and consequently needs further purification [20].

### 2.3.2 TMA doping of liquid argon / liquid xenon mixture.

Although liquid argon can be doped directly using TMA, it is advantageous to add LXe at a concentration of around 100-150 ppm.

UV light emission of (LAr - LXe)* excited states, as mentionned earlier,
present the wavelength of the LXe scintillation light, or very close to it. While the ionization potential of allene is too high for producing any photoelectron, TMA presents at this wavelength the highest quantum efficiency for photoionization of all compounds, nearly 100%. LXe doping will also insure an overall fast decay time of the scintillation light.

On the other hand, TMA is a large molecule, probably not very radiation resistant. In addition this compound is known to be sticky, and hard to remove from walls and electrodes once it has been put in experimental cells. That could be a major drawback in using TMA.

2.4 General remarks.

Going away from the use of pure noble gas brings several complications. The first one is the radiation damage. Behaviour of dopants under such a severe radiation environment like LHC is essentially unknown. Break-up of these molecules will modify charge collection and drift velocity. Furthermore, impurities from the dopants can be very harmful. The level of purity required may be much higher than in the case of pure liquid argon. That would have important constraints on the technology, materials used and purification. One solution toward monitoring precisely the presence of impurities will be treated in Section 4.

Another main concern is the one of reaching and monitoring the uniformity of the mixture. Homogeneity can be best achieved by adding the dopant after first liquefaction of part of the required volume of argon in the detector as described in [19]. A stable concentration of the dopant is then certainly difficult to reach entirely due not only to the severe dependence of its solubility in the liquid argon with temperature (especially concerning the allene having a melting point of -136°C) but also to the inevitable presence of a gas phase sitting above the liquid phase. The volume of the gas pocket on top of the liquid should be minimized to insure the smallest possible concentration of dopant in it.
3. DESCRIPTION OF THE TEST SET-UP AND MONITORING.

3.1 Introduction.

In case of doped liquid argon several parameters have to be measured:

- the collected charge
- the drift velocity
- the lifetime of the mixture

These parameters depend on the dopant concentration as well as on the amount of impurities dissolved in the liquid. In order to measure these parameters three main solutions are available: radioactive sources, photoproduction of free electrons in the drift gap by a UV Laser and as far as impurity and dopant concentrations are concerned IR spectroscopy. The last one is described in the next Section.

The effect of the dopants as a function of the ionization density can be evaluated with $\alpha$ and $\beta$-particles. For the present test set-up we plan to use both sources, $^{241}$Am for $\alpha$-particles and $^{207}$Bi for electrons, placed in the same volume of liquid. We will measure the amount of recombination by comparing $\alpha$ and $\beta$ as a function of dopant concentrations, and we will compare the charge gain due to the photosensitive substances. $dE/dx$-saturation properties and the determination of the value of the Birk's constant for different compounds at different concentrations will also be measured.

In addition to radioactive sources, use of an UV Laser extracting free electrons from a photocathode facing the drift gap has many advantages, as demonstrated by the ICARUS group, Fig.8. All details concerning it can be found in Ref [9]. The UV Laser provides a much higher number of primary electrons extracted from the photocathode ($=10^6$ electrons) compared with the much smaller signals given by the radioactive sources, permitting sensitive pulse-shape
3.2 Description of the set-up.

The set-up is shown in Fig. 9. A double-grid chamber is used for the observation of the UV Laser-induced electrons. The drift time separating the two grids provides a direct measurement of the drift velocity for a given electric field. Fig. 10, extracted from the ICARUS work, shows the pulse shapes from the cathode and the anode for the Laser pulse as well as the corresponding distributions of lifetimes after processing of the data, for two cases: unpurified and purified liquid argon.

The ratio between the pulse heights, or charge collected at the cathode and the anode, is a very easy measurement of the lifetime of charge in the liquid using the approximate formula:

\[
\frac{Q(\text{anode})}{Q(\text{cathode})} \approx \exp\left(-\frac{t_d}{\tau}\right),
\]

where \(\tau\) is defined as the "liquid" lifetime. This lifetime has been shown to be inversely proportional to the amount of impurities [22]. With such a set-up, few Laser pulses only are necessary to obtain a precise measurement of the drift velocity and liquid lifetime.

In our case, as we want to approach as much as possible the real conditions of an LHC calorimeter, we intend to work at a much higher field than the ICARUS collaboration and for that reason we have to redesign parts of the cell. With a 2 cm drift gap the range of lifetimes probed - few \(\mu\)s to few tens of \(\mu\)s at nominal electric field - is adequate for our use. Observation of higher lifetimes will guarantee a negligible loss of electron collection in small calorimeter gaps.

Radioactive sources are of course still necessary as the Laser set-up does not give any information concerning primary ionization of the liquid itself. Values of electric field of 10 kV/cm are also used to drift ionization electrons from \(\alpha\) and \(\beta\) particles. Concerning the \(\beta\) source a single grid ionization chamber is adequate with a 1 cm drift gap, sufficient to contain \(~1\) MeV radiation from the \(^{207}\)Bi. In this case
a grid chamber is necessary in order to be independant of the direction of emission of the β particles.

Concerning $^{241}$Am α-particles, a double grid chamber is used as in the UV Laser case in order to try to perform the same measurements. We aim with the source, although signals are much smaller than in the Laser case, to measure not only the collected charge but as well the drift velocity and the lifetime. Comparison with the precise values given by the Laser cell will allow us to verify to what extend similar results can also be obtained with the source. In the case of a 4π calorimeter we expect to use only radioactive sources placed at several places inside the device with the aim to calibrate and monitor the calorimeter in situ with α and β sources and to perform the measurements of all necessary parameters.

A detailed drawing of the set-up is given in Fig. 11 a and b. It includes 30 kV and 15 kV feedthroughts necessary to reach a field of 10 kV / cm in the drift gap. The photocathode, grids, electrodes and UV fiber feedtroughs are similar to the ones developed by the ICARUS collaboration. At the bottom of the pot, a flange is foreseen allowing in due time to add a section for IR absorption measurements containing IR windows on each side of the optical path.

### 3.3 Purification system.

We intend to build a small liquid argon and dopant purification system shown in Fig.12, which is derived from the existing UA1 purification system used for the production of ultrapure warm liquid for calorimetry [22,23]. As the volume of our test chamber is small, the system will remain at a moderate scale and will essentially include an Oxisorb cartridge for removal of oxygen on the argon line starting from Ar N60, to the extent that CO, CO$_2$ are unimportant scavengers in the system. The set-up at the Manne Siegbahn Inst., Stockholm, will include in addition a Ti-getter in the argon line. After purification using molecular sieves, the dopant can either be mixed with argon in a special reservoir before liquefaction or transferred directly in the test cell. Different ways of mixing allene and LAr are described in [19]. Temperatures of the test cell around liquid argon would
preferably be obtained by a cooling system instead of a liquid argon bath in order to provide more flexibility.

3.4 Associated electronics and readout.

Although first tests will be performed with a digital scope, one envisages the readout schemes shown in Fig.13a-d.

The preamplifiers are the ones developed for the UA1 or ICARUS experiments [24]. They have a rise time of 50 ns and adequate dynamic range. The overall response of the electronics will be measured with test pulses sent to the input of the preamplifiers via a 1 pF capacitor. Fig. 14 gives the basic scheme of the HV distribution for a given channel, including test and blocking capacitor.

Careful study of the pulse shapes recorded by waveform digitizers will provide another precise measurement of the "liquid" lifetime and drift speed of electrons [25]. As mentioned earlier, these come either from direct ionization of the liquid or from photoemission by the dopant, if photosensitive. By this method it will be possible to measure delayed signals coming from any remaining slow decay component of the LAr luminescence.

We intend to process also the signals from the ionisation chambers through a separate fast amplifier system with bipolar shaping [6] developed for high rate data acquisition. A direct comparison between slow and fast responses of the signals from Laser, α and β sources will provide useful information on the performance achievable with such a high speed system. In addition a study of the energy resolution as a function of the rise-time of the pulse will be performed using a parallel plate gridded ionisation chamber.

We plan to control laser firing, calibration pulses and DAQ via a MAC-CC connected to a MACINTOSH computer.
4. INFRARED ABSORPTION SPECTROSCOPY AS DIAGNOSTICS OF IMPURITIES AND DOPANT.

4.1 Justification.

Measurement of the lifetime of the liquid mixture is certainly sensitive to dissolved impurities. While the global amount of impurities can be estimated from the value of the lifetime, no information can be gotten on the types of impurities such as oxygen, CO₂, CO, other more complex molecules or halogens. Such information is necessary if one wishes to isolate the origin of the impurity. Sources of impurities could be the argon itself, the dopant or components of the calorimeter, such as preamplifiers, honeycomb or PC-boards. Moreover, monitoring of the amount of dopant and of its possible decomposition during an irradiation test could be a unique tool in evaluating the behaviour of such substances under the LHC radiation environment. This kind of monitoring will have to be performed in situ, namely with the liquid in the test cell. IR absorption spectroscopy allows to perform such an analysis under all these constraints.

IR absorption spectra of most gases are known, including methane, allene (propadiene), CO₂, CO, hydrocarbons and halogens [13]. The sensitivity of the IR absorption techniques is considerably improved in the case of liquefied gases. Effectively the liquefaction of a gas increases the molecular density of the impurities making its detection easier. Molecular densities in liquids are ≈ 2 × 10²² molecules / cm³. A 1 ppm level of an impurity translates into ≥ 10¹⁶ molecules / cm³ of impurity in solution, much above the molecular density in the gas phase.

An other advantage resides in the simplification of the absorption spectra in the liquid phase at such low temperatures. First of all, the absorption wavelengths of infrared bands of dissolved compounds are usually very close to those of their vapors so the large amount of published data for infrared absorption of gases can be used as a guideline. Secondly, a liquefied solution, at low temperatures, has much simpler spectra. Effectively, molecular rotation is suppressed, so the complex rotational structure of a solute vibrational band usually collapses to a single, sharp
peak, which is stronger than for the gas at room temperature. Provided that the liquefied solution (liquid argon with methane, allene or TMG for example) is essentially free of infrared absorptions at wavelengths where the impurities absorb, detection of low levels (ppm - ppb) of impurities can be performed.

4.2 Two examples from the litterature.

To our knowledge, several examples for quantitative detection of impurities in cryogenic solutions by IR spectroscopy have been published. In one of them the cryogenic carriers were liquid xenon and liquid air [11], in another liquid argon and liquid xenon were used [12]. We recall here the main results and conclusions obtained by these authors as an example. Other compounds mixed with cryogenic liquids have also been analysed [26].

S.M.Freund et al. [11] used an IR optical pathlength of 1.3 cm and 2.6 cm in liquid xenon and liquid air respectively. Using commercial spectroscopic grade liquid xenon, they isolate an absorption peak corresponding to about 2 ppm of CO\textsubscript{2} in the sample, as shown in Fig. 15. The good-signal-to-noise ratio observed for these CO\textsubscript{2} levels suggests that a factor of 100 reduction in CO\textsubscript{2} concentration could be measured quantitatively with the same apparatus and conditions, namely around 20 ppb concentration. A longer IR pathlength would even further improve the limit of detection.

The suppression of the rotational structure of molecules is demonstrated by the same authors by analysing mixtures of CF\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{2}H\textsubscript{3}Cl dissolved in liquefied air. Fig. 16 extracted from their paper demonstrates that the bands of the molecules in solution are completely resolved whereas little qualitative or quantitative information can be derived from the vapor phase spectra.

In their publication, C.R.Gruhn and W.B.Maier II [12] used pathlengths of 2.6 cm and 1 m for impurities detection in liquid argon and liquid xenon. Fig. 17 shows the IR absorption spectrum through 1 m of liquid argon N60. The corresponding molefractions to the absorption peaks are 0.1, 1.2 and 100 ppm of
CO₂, CO and O₂. Again the beautiful separation of the CO₂ peaks suggests that a
very high sensitivity can be obtained. For example a factor 10 smaller
concentration could still be observed, which would bring the sensitivity to
approximately 10 ppb.

In both experiments Perkin-Elmer model 180 spectrometers were used.
The very sharp peaks observed in liquified solutions call effectively for such a high
resolution apparatus.

In conclusion one can deduce from these two measurements that clean IR
absorption peaks can be detected and measured down to a level of about 10 ppb
depending of the IR optical pathlength. That is adequate for the level of impurities
we need to monitor in a future calorimeter; such a level of impurities would be
compatible with lifetimes in excess of 50 μs which is entirely sufficient for these
needs.

4.3 Detection of expected impurities.

In the previous section we have shown that the sensitivity of the IR
absorption method is perfectly adequate to measure the harmful impurities with
appropriate sensitivity. One general condition has to be met however, namely that
the IR absorption peaks do not coincide with the IR absorption peaks of the dopant
itself, allene, methane.

This last point is difficult to assert as neither allene, methane nor the
impurities except CO₂, CO and O₂ have been studied in cryogenic solutions with IR
spectroscopy. The absorption spectrum of the allene for example as a gas certainly
shows a very complicated structure with many absorption peaks between 2 - 20 μm
[11]. Methane shows a much simpler structure essentially concentrated around a
broad peak near 1250 nm⁻¹. It is not known however to which extend the
simplification of the rotational structure of the dopants and impurities will be such
that they can be separated. We consider this part as a research project in
collaboration with other specialized CERN departments given the fact that so little
is really known in IR absorption peaks of such substances in cryogenic liquids.
The question of the IR windows on each side of the optical pathlength is not trivial although it was already solved in the two mentioned publications. They should be transparent between 2 - 20 \( \mu \text{m} \), should be operational at liquid argon temperature, should stand thermal shocks, be hopefully easily mountable on CONFLAT flanges, be bakeable at reasonable temperatures. We are presently investigating different materials like BaF\(_2\) (although its cut-off is only around 10 \( \mu \text{m} \) and not 20 \( \mu \text{m} \)), CsI (unfortunately hygroscopic, but resistant to temperature changes), KRS-5 and AgCl.

Help from special technologies departments at CERN is requested in order to succeed in installing such delicate IR windows as well as for the overall use of the IR spectrometer.

We wish to emphasize that such an IR spectrometer represents a CERN wide project due to its multiple possibilities in gas, powder, liquid and material analysis. Justifications for such an instrument, outside the present project, are described in [27]. We would request to have the instrument on loan on the CERN site during this development in collaboration with the concerned Division.

5. CONCLUSION.

We propose to build a set-up able to measure the physical parameters related to the charge collection in ionization chambers, such as charge, speed of charge collection and lifetime of the liquid. In a single liquid volume, two gaps will be equipped with \( \alpha \) and \( \beta \) radioactive sources\(^{241}\) Am and \(^{207}\) Bi. The third gap uses a UV Laser extracting electrons from a photocathode.

This set-up will allow us to search for the best additive and its optimal concentration to the pure liquid argon in order to increase the drift speed of the electron response by a factor 2 at least, while still collecting the same charge. That is essential considering the very high rate of interactions at LHC. The set-up will be used also to define the best monitoring for a future calorimeter at LHC with the
We propose also to develop in collaboration with Special Technology Departement at CERN the use of an IR spectrograph which will permit to determine the nature and amount of the impurities dissolved in the mixture, as well as the percentage of additive in solution. Its role in helping the understanding of radiation damage by spectroscopy of the decay products is also stressed.

Such complete information is necessary in order to understand the features associated with the use of novel dopants in liquid argon. The associated difficulties on a large scale project can then be evaluated, helping to decide the correct way to take for future successful operation.

The proposed set-up could also be used for studies involving liquid krypton or liquid xenon.

Details of budget request, timescales and sharing of responsibilities can be found in Appendix A, B and C.

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APPENDIX A : BUDGET AND MANPOWER CONSIDERATIONS

1) Manne Siegbahn Inst. of Physics, STOCKHOLM

The MSI, Stockholm, has build an ultra-clean gas handling and purification system involving a Ti-getter and an ion-pump. This system is able to purify 300 liters / s and will be ready to perform tests not only with liquid argon but also with liquid xenon which represents a unique facility. In particular it will allow the doping of liquid argon and of liquid xenon. This very complete station is estimated at 250 kSFr and will be available at Stockholm in the context of the present collaboration.

Within the context of basic R & D of liquid Argon and liquid Xenon detectors, the group in Stockholm will apply for a contribution of 400'000 SFr from the Swedish Natural Research Council and/or the Swedish Technical Research Council.

2) CERN

The apparatus at CERN is entirely new. Although we hope to recuperate certain parts from existing equipment, some items will still have to be bought or build.

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<td>Test cell with ionization chambers including Laser fiber</td>
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<th>b) CRYOSTAT / PURIFICATION / VACUUM INSTRUMENTS</th>
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<td>Vacuum tank</td>
</tr>
<tr>
<td>Refrigeration system</td>
</tr>
<tr>
<td>Valves (~10 NUPROS, 4 VATs, 1 DN150CF, 1 cold automatic)</td>
</tr>
<tr>
<td>2 OXYSORB large model 10 bars</td>
</tr>
<tr>
<td>Dewars for liquid nitrogen CD 45-90</td>
</tr>
<tr>
<td>Pressure transducer including controller</td>
</tr>
<tr>
<td>Mass flow meter/controller</td>
</tr>
</tbody>
</table>
Pirani and Penning gauges set for vacuum measurement 3'000
Piping, vacuum connections 7'000
Construction 5'000

c) HV DISTRIBUTION
HV distribution box including material 4'000
HV feedthroughs, 30kV and 15 kV 3'000
Fast waveform digitizer 10'000
Front-end readout infrastructure 2'000
Electronics pool rental fee 10'000

d) LIQUID AND DOPANT GAS
Liquid Argon 7'000
Dopant gas bottles (allene, propene, TEA, TMG) 7'000
Contingency 8'000

Travel 10'000

TOTAL 170'000

The present budget request covers the period 1990 - 1991.
To the extend that MAC-CC, MAC INTOSH, CAMAC crates can be borrowed from existing experiments, we would only need to get from electronic-pool modules like:
- peak-sensing ADC, TDC, qVt
- NIM shaping-amplifiers, discriminators and gates.

In terms of manpower, two technicians are needed in addition to the physicists involved:
- a vacuum / cryogenic specialist
- electronics
initially for a period of one year.
3) UV LASER

Initially, we will be able to borrow a UV Laser. In the long term however, should such a device be continuously needed, one should envisage to buy one (= 60 kSFr). In that case we would present an additional request together with a progress report.

4) FT-IR SPECTROGRAPH

A spectrograph like a Perkin-Elmer model 1760 or a Bruker model IFS 66 cost around 200 kSFr., including some specific software packages for the PC. It is expected to be financed from the MT divisional budget.
APPENDIX B: MILESTONES AND TIMESCALE

This Appendix describes the foreseen timescale to build and test the new set-up at CERN.

CONSTRUCTION:

Construction of the test cell with ionization chambers : Aug 90
Construction of the additional cell for IR spectroscopy : Oct 90
Delivery of the IR spectrometer : Dec 90
Reception of the IR spectrometer : Beg 91

The next construction milestones are indicated relative to a time zero following budget approval.

Construction of the installation (vacuum, lines, bakeout) : 2 months
Construction of the vacuum tank : 2 months
Cooling system : 4 months

TESTS:

Start of debugging the test cell in pure LAr : Aug 90
Start investigations with dopants : Sept 90

Some timescales are indicated relatively to a time zero following budget approval.

Switch from LAr bath to cryostat : 4 months
IR spectrometer operational for absorption measurements : 2 months
First results from dopant tests : 3 months
Complete tests : 12 months
APPENDIX C: RESPONSABILITIES

CERN:

- investigation of single additives, mainly such as methane and allene, to liquid argon using the proposed test set-up based on ionization chambers (binary mixtures)

- development of the IR spectroscopy techniques in view of monitoring the presence of impurities and the content of additive

- study of the radiation damage on the mixture of LAr and dopant

MANNE SIEGBAHN Inst. of Physics, STOCKHOLM:

- purification studies using a Ti-getter

- investigation of the time dependence of the liquid argon luminescence intensity in presence of additives such as photoscintillation dopants or/and liquid xenon and its correlation with ionization signals (binary and tertiary mixtures)

- conduct similar studies on LXe

- study of energy resolution in function of timing of the pulse using parallel plate gridded ionization chamber
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LIST OF FIGURES

Fig.1 : Signal response of a detector-amplifier system for different charge collection times [6].

Fig.2 : The electron drift velocity of pure liquid argon, argon / methane and argon / ethylene mixtures [7].

Fig.3a : Results on hadronic energy resolution from the NA34 experiment (HELIOS calorimeter) using protons. The point with 0.35% methane doping has been obtained with 100 GeV/c protons. A gain of signal consistent with an increase in drift velocity of approximately a factor two was observed.

Fig.3b : Results on e/π ratio from the NA34 experiment (HELIOS calorimeter) using protons. The point with 0.35% methane doping has been obtained with 100 GeV/c protons.

Fig.4 : Time dependence of the luminescence intensity for liquid argon without and with an applied electric field.

Fig.5a : Time dependence of the luminescence for Xe-doped liquid argon excited by electrons.

Fig.5b : Time dependence of the luminescence for N₂-doped liquid argon excited by electrons.

Fig.6a : Charge collected as a function of electric field for 5.5 MeV alpha particles in pur LAr and in LAr with a variety of dopants [18].

Fig.6b : Charge collected as a function of electric field for 5.5 MeV alpha particles in LAr when doped with TMG and allene [18].

Fig.7 : Collected charge vs applied electric field E for alpha particles in allene
doped liquid argon and pure liquid argon [19].

Fig. 8: A cross-section through the test chamber developed by the ICARUS collaboration [9].

Fig. 9: Arrangement of the cells of the test set-up. All three cells, $^{241}$Am source, $^{207}$Bi source and Laser are within the same volume of liquid for direct comparison.

Fig. 10: a) Typical induced signals of the drifting electrons observed on the cathode and anode, seen on the oscilloscope for:

\[ \text{Argon 60 (V.B.}_{\text{cat.}} = 200 \text{ mV/cm, V.B.}_{\text{an.}} = 20 \text{ mV/cm,} \]
\[ \text{T.B.} = 10 \mu\text{sec/cm, } E_{G1-G2} = 400 \text{ V/cm} \]

b) Electron lifetime $t$ (μs) at $E = 384$ V/cm for Argon 60

c) Typical induced signals of the drifting electrons of the cathode and anode seen on the oscilloscope for:

\[ \text{Argon 60 + OXISORB (V.B.} = 100 \text{ mV/cm, T.B.} = 10 \mu\text{sec/cm,} \]
\[ E_{G1-G2} = 400 \text{ V/cm} \]

d) Electron lifetime $t$ (μs) at $E = 384$ V/cm for Argon 60 + OXISORB

From Ref. [9].

Fig. 11a: Top plate of the test chamber, showing external diameters of HV feedthroughts. Internal electrodes and MACOR supports are shown as shaded.

Fig. 11b: Cross-section of the test chamber.

Fig. 12: Scheme of the purification system for liquid argon and additive.

Fig. 13: Electronics and read-out system for the test ionization chambers.

13a, 13b: Laser cell measuring set-up, receiver and signal conditioning.

13c, 13d: α-source cell measuring set-up, receiver and signal conditioning.
Fig.14: Connections of HV, test capacitor and input to preamplifier for a given channel of the test set-up.

Fig.15: Infrared spectrum of 6 ppm CO$_2$ dissolved in liquid Xe and that of commercial liquid Xe showing a 2 ppm CO$_2$ impurity level [11].

Fig.16: Infrared spectra of complex mixtures showing the differences between room temperature and liquid-air temperature. The simplification of the spectra is striking [11].

Fig.17: Infrared absorption spectrum through 1 m of liquid argon N60 [12].
<table>
<thead>
<tr>
<th>Material (^d)</th>
<th>(I_g) [^{[eV]})^a</th>
<th>Dipole [^{[debyes]})^b</th>
<th>Estimated [^{[90 K] [Torr]})^b</th>
<th>Charge collected[^c) (^{(LAr = 1)})</th>
<th>Concentration [^{[ppm]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>((C_2H_5)_3N)</td>
<td>7.50</td>
<td>0.66</td>
<td>2.2</td>
<td>1.3</td>
</tr>
<tr>
<td>TMA</td>
<td>((CH_3)_3N)</td>
<td>7.82</td>
<td>0.612</td>
<td>3.4</td>
<td>1.6</td>
</tr>
<tr>
<td>TMT</td>
<td>((CH_3)_4Sn)</td>
<td>8.25/8.76</td>
<td>-</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>(C_6H_{10})</td>
<td>8.95</td>
<td>-</td>
<td>2.1</td>
<td>1.3</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>(C_4H_6)</td>
<td>9.06</td>
<td>0</td>
<td>4.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Cis &amp; Trans 2 butene</td>
<td>(C_4H_8)</td>
<td>9.13</td>
<td>0 (trans)</td>
<td>3.6</td>
<td>1.6</td>
</tr>
<tr>
<td>TMG</td>
<td>((CH_3)_4Ge)</td>
<td>9.2/9.29</td>
<td>-</td>
<td>7.4 (9.8)</td>
<td>2.6 (2.7)</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>(C_4H_8)</td>
<td>9.23</td>
<td>0.5</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>(CH_3SH)</td>
<td>9.44</td>
<td>1.52</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Pentene (technical)</td>
<td>(C_5H_{10})</td>
<td>9.5</td>
<td>-</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Allene</td>
<td>(C_3H_4)</td>
<td>9.53</td>
<td>0</td>
<td>6.5 (8.7)</td>
<td>2.5 (2.7)</td>
</tr>
<tr>
<td>TMS</td>
<td>((CH_3)_4Si)</td>
<td>9.86</td>
<td>0.525</td>
<td>4.6</td>
<td>1.8</td>
</tr>
<tr>
<td>DME</td>
<td>((CH_3)_2O)</td>
<td>10.0</td>
<td>1.30</td>
<td>3.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\(^a\) Ref. [9].

\(^b\) Ref. [10].

\(^c\) ( ) Purified LAr used.

\(^d\) Triethyamine (TEA), Trimethylamine (TMA), tetramethyltin (TMT), tetramethylgermanium (TMG), tetramethylsilane (TMS), dimethylether (DME).
Table II: Quantum Efficiency for Photoionization

<table>
<thead>
<tr>
<th>Liquid</th>
<th>C</th>
<th>σ</th>
<th>( l_p )</th>
<th>( \phi )</th>
<th>field region</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAr + allene</td>
<td>25 ppm</td>
<td>25 Mb</td>
<td>0.076 cm</td>
<td>0.55</td>
<td>3～10 kV/cm</td>
</tr>
<tr>
<td>+ TMA</td>
<td>100 ppm</td>
<td>50 Mb</td>
<td>0.0095 cm</td>
<td>0.23</td>
<td>5～8 kV/cm</td>
</tr>
<tr>
<td>+ TEO</td>
<td>200 ppm</td>
<td>(50 Mb)</td>
<td>0.0047 cm</td>
<td>0.15</td>
<td>3～6 kV/cm</td>
</tr>
<tr>
<td>+ ethylene</td>
<td>155 ppm</td>
<td>(50 Mb)</td>
<td>0.0061 cm</td>
<td>0.18</td>
<td>5～8 kV/cm</td>
</tr>
<tr>
<td>LXe + TEO</td>
<td>50 ppm</td>
<td>15 Mb</td>
<td>0.098 cm</td>
<td>0.75</td>
<td>4 kV/cm</td>
</tr>
<tr>
<td>+ TMA</td>
<td>55 ppm</td>
<td>(15 Mb)</td>
<td>0.089 cm</td>
<td>0.75</td>
<td>0.5～6 kV/cm</td>
</tr>
<tr>
<td>+ 6 ppm</td>
<td>6 ppm</td>
<td>0.82 cm</td>
<td>0.95</td>
<td>2～4 kV/cm</td>
<td></td>
</tr>
<tr>
<td>+ 1 ppm</td>
<td>1 ppm</td>
<td>4.9 cm</td>
<td>&gt;1.0</td>
<td>0.3～7 kV/cm</td>
<td></td>
</tr>
<tr>
<td>+ 7 ppm</td>
<td>7 ppm</td>
<td>0.70 cm</td>
<td>~1.1</td>
<td>0.5～6 kV/cm</td>
<td></td>
</tr>
<tr>
<td>+ 1 ppm</td>
<td>1 ppm</td>
<td>4.9 cm</td>
<td>&gt;0.70</td>
<td>0.5～7 kV/cm</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 1
FIGURE 2
e / π ratio [ NA34 ]

Beam energy [ GeV/c ]

- □ pure Ar
- ◆ 0.35% CH4

FIGURE 3b
FIGURE 4
FIGURE 5a
FIGURE 5b
FIGURE 6a

FIGURE 6b
FIGURE 7

Liq. Ar + allene
Method 'A'

- x 250 ppm
- △ 11 ppm
- □ 82 ppm
- ○ pure
+ 21 ppm

Collected Charge \( Q/Q_0 \) (%)

Electric field \( E \) (kV/cm)
FIGURE 8
**FIGURE 10**

**Electron lifetime**

**Argon 60**

Cathode  \( V_{\text{cat}} = 516.7 \text{ mV} \)

Anode  \( V_{\text{an}} = 17.5 \text{ mV} \)

\[
\tau = (12.4 \pm 0.4) \mu\text{sec}
\]

"Ar 60"

**Argon 60 + OXISORB**

Cathode  \( V_{\text{cat}} = 350 \text{ mV} \)

Anode  \( V_{\text{an}} = 233 \text{ mV} \)

\[
\tau = (95.9 \pm 13.8) \mu\text{sec}
\]

"Ar 60 + OXISORB"
TOP VIEW

DN 200

ELECTRODE

FILLING PIPE

SUPPORT RING

MACOR

FRIALIT 551-0260

VACUUM GENERATORS EFT34A

HV FEEDTROUGHS

FIGURE 11a
CROSS-SECTION VIEW

α SOURCE CHAMBER

β SOURCE CHAMBER

LASER CHAMBER

SUPPORT RING

MACOR

UV FIBER FEEDTHROUGH

FIGURE 11 b
D-LAr RECEIVER-SHAPER AND SIGNAL CONDITIONING
α - SOURCE

FIGURE 13d
D-LAr ALPHA SOURCE MEASURING SET-UP

CALIBRATION

RECEIVER-SHAPER AND SIGNAL CONDITIONING

ANALOG INPUT

ANODE GATE

ANALOG OUTPUT

CATHODE GATE

1pF

ANODE

- - - - - -

500pF

ALPHA SOURCE

CATHODE

- - - - - -

500pF

CURRENT INTEGRATOR

START

STOP

CAMAC - BUS

ADC

ADC

TDC

FIGURE 13c
Figure 2. Infrared spectrum of 6 ppm total CO₂ dissolved in liquid Xe at −110°C (curve I) and that of the commercial LXe used, which has about 2 ppm CO₂ impurity (Curve II).

Figure 3. Infrared spectrum (curve I) of the mixture of CCl₂F₂ (0.3 ppm; features at 917.5 and 886.5 cm⁻¹) and C₂H₃Cl (2 ppm; features at 943.0 and 899.0 cm⁻¹) dissolved in liquid air at −188°C, and spectra of 25°C mixtures of 10 Torr CCl₂F₂ and 100 Torr of C₂H₃Cl (curve II) and 10.6 Torr of CCl₂F₂ and 6.8 Torr of C₂H₃Cl (curve III).