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Development of a gadolinium-loaded liquid scintillator for solar neutrino detection and neutron measurements

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Abstract

A high flashpoint, low-toxicity liquid scintillator based on α -hydroxytoluene and containing 10 wt% Gd has been developed for solar neutrino detection and neutron measurements. Dissolution of the gadolinium compound into the scintillator was facilitated by the use of the extractant triethylphosphate. Preliminary investigation has shown the attenuation length of the loaded scintillator to be 1.42 m at 420 nm and the light collection to be 30% of that produced by an unloaded sample.

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1. Introduction

Liquid and plastic scintillators loaded with additional elements are extensively used in physics instrumentation. Boron- and gadolinium-loaded scintillators provide high-sensitivity neutron measurements. Gd-, Yb- and In-loaded scintillators have been proposed for real-time, low-energy solar neutrino detection [1] and scintillators based in 1- and 2-methylnaphthalene have been heavily loaded by Raghavan [1]. Nemtchenok et al. [2]

succeeded to load 1-methylnaphthalene with 86 g of Gd/l using an organophosphate extractant and Barabanov et al. [3] have loaded Ytterbium chloride at 88 g/l into a pseudocumene-based scintillator using triisooamylphosphine oxide.

To ensure high-efficiency neutron detection, typically 0.1–1.5% of Gd by weight is required (see, for example, Refs. [4–6]). For a detector to be sensitive to solar neutrinos, a target mass of about 10 tons of Gd/Yb/In is necessary, which is achievable only with a high fraction of loaded element. At present only scintillators with up to 1.5% Gd are commercially available [6]. Although both CHOOZ [4] and Palo Verde [5] did succeed in preparing a 0.1 wt% gadolinium-loaded scintillator with high attenuation length and reasonable

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stability, the manufacture of a 10% loaded sample is by no means a simple development of their work.

Stability of the loaded scintillator is another crucial issue. This is particularly important for long-term experiments, designed to study low-energy solar neutrinos or to measure neutrino fluxes from galactic supernovae via neutral current excitation of heavy (lead) nuclei followed by the release of neutrons, which can be detected by a loaded scintillator (see Ref. [7] and references therein for a description of the OMNIS project).

In this paper we will describe the development of a Gd-loaded liquid scintillator intended for use in the Boulby underground laboratory (Boulby mine, North Yorkshire, UK, vertical depth—1070 m or 2800 m water equivalent). The site is currently used for dark matter detection but several proposals for an extension of the scientific programme into neutrino astrophysics are being discussed. These include a new real-time, low threshold, spectroscopic solar neutrino detector SIREN (Solar neutrino Interactions by Real time Excitation of Nuclei) [8] and a supernova neutrino detector OMNIS [7]. SIREN is based on the ideas developed by Raghavan [1], and is similar to LENS [9]. The discussed scintillator should satisfy the safety requirements of the working mine.

Although with the new results of the SNO [10] and KamLAND [11] experiments the solar neutrino deficit can be explained by the large mixing angle MSW oscillations [12], accurate, real-time measurements of the solar neutrino spectrum at low energies are still vital for precise testing of solar models [13] and for the search for second-order (subdominant) effects in neutrino oscillations [14]. Thus, the preparation of large quantities of stable, safe, liquid scintillator loaded with a high fraction of a rare-earth element remains an important task. Several other groups are also working on this problem [1,15,16].

In our studies we concentrated on Gd-loaded scintillators for practical reasons. Gd is reasonably cheap, certainly cheaper than Yb or In, and is convenient in the development process. Its chemical properties are similar to other rare-earth elements and the technique developed for Gd,

can also be used in the preparation of scintillators with different loaded element.

2. Choice of scintillator base

Our research and development concerns a detector suitable for installation in deep underground sites, for instance in Boulby mine, North Yorkshire in an area occupied by dark matter detectors. This imposes additional safety requirements beyond those for surface-based experiments with scintillators. The scintillator must be of low toxicity and chemical activity, and the flashpoint of all liquids must exceed 100°C. Xylene- and dioxane-based scintillators are therefore not suitable.

To decrease the deleterious effect of the background from natural radioactive isotopes present in the scintillator, the mass ratio of target-to-scintillator should be maximised without significant loss of scintillator transparency and light yield. From 5% to 10% of gadolinium by weight should be loaded into the scintillator to make it useful for solar neutrino detection. At present only 0.5–1.5% gadolinium-loaded scintillators are commercially available. The difficulty of increasing this emerges from the fact that commercially available gadolinium compounds are all insoluble in commonly used liquid scintillation bases. Gadolinium is soluble in low molecular weight solvents, but these lower the flashpoint (fp) below the 100°C minimum safety level and decrease the light yield. Although the miscibility of these solvents with some liquid scintillator bases is good, the best scintillators such as pseudocumene have low fps (fp 52°C) and are also too toxic for mine use. Our current attempts are, therefore, concentrated on the preparation of loaded scintillators based on phenylxylylene (fp 120°C), methylnaphthalene (fp 82°C), α -hydroxytoluene (fp 93°C) and diisopropylnaphthalene (fp 150°C). All have been shown to produce good light yield in their unloaded form (greater than 60% of anthracene), as well as good transparency (attenuation lengths in excess of 10 m). All liquids with the exception of α -hydroxytoluene can be purchased from Zinsser Analytic Ltd. at scintillation grade purity. α -

hydroxytoluene was supplied by Sigma-Aldrich and purified by vacuum distillation.

3. Manufacture of 19% Gd-loaded extractant

Lanthanides such as gadolinium are particularly susceptible to forming complexes, in which the atom or ion is surrounded by a number of oppositely charged ions or neutral molecules, all possessing lone pairs of electrons which are available for donation to the vacant orbitals of the atom or ion. These complexing agents are known as ligands arranging themselves about the central ion in such a way as to be as far as possible from each other, establishing a stable distribution of electrons. Gadolinium nitrate hexahydrate is surrounded by six water molecules (ligands) in an octahedral arrangement. In this state gadolinium nitrate is completely insoluble in all the organic scintillators. During dissolution in an organic scintillator, a dynamic equilibrium exists between the free ions present in the solution and the undissociated electrolyte. Although the dissociation constant of this equilibrium is fixed for a particular temperature, altering the type of ligand can effectively increase the extent of dissociation with the effect that the solubility of gadolinium within the base will significantly increase.

Gadolinium compounds are known to complex with neutral organophosphate ligands, trivalent lanthanide cations forming a trisolute [17] when extracted by alkyl phosphates. Alkyl phosphates were selected because of their stability and reluctance to undergo hydrolysis during the extraction process forming gadolinium hydroxide with the water molecules ejected from the original complex. Substitution of the water ligands for triethylphosphate molecules during dissolution dramatically increases the solubility of gadolinium compounds in organic scintillators.

An excess of gadolinium nitrate hexahydrate was added to triethylphosphate and agitated at 40°C under nitrogen for 24 h. The inclusion of water within the final loaded scintillator was far from desirable. Water and most polar impurities act as quenching agents within the scintillator decreasing light yield via non-radiative deactivation

of the excited molecules of the scintillator which would otherwise have dissipated their energy by photon production. The mixture was therefore centrifuged and the organic phase separated from the aqueous phase by decanting. The gadolinium complex was then concentrated and purified by vacuum distillation.

An excess of gadolinium nitrate hexahydrate was once again added to this organic phase and the process repeated. At some point during vacuum distillation, the proportion of gadolinium-loaded within triethylphosphate increased to a concentration exceeding the supersaturation limit, a white suspension of small feather-like crystals forming and the sample becoming completely opaque. At this point a small quantity of triethylphosphate was added to dissolve the precipitate and the solvent was said to be fully loaded. Heavily loaded triethylphosphate has the appearance of an oily liquid. The aqueous phase, separated by centrifuging, was weighed and then evaporated in a 250 ml Apollo evaporator flask. No residue was detected suggesting that the gadolinium compound had been completely absorbed by the triethyl phosphate. An Ohaus TS series balance with a readability of ± 1 mg was used for all component weights. Because of the accuracy with which the measurements could be taken the percentage loading could be very precisely determined. Gadolinium loading of up to 19 wt% ($\text{Gd}(\text{NO}_3)_3 \cdot 3\text{TEP}$) was achieved.

4. Manufacture of 10% Gd-loaded scintillator

Pure liquid scintillators based on phenylxylylene, methylnaphthalene, α -hydroxytoluene and diisopropylnaphthalene were prepared by mixing the range of bases with a variety of fluors (4 g/l) and wavershifters (0.3 g/l). The main criteria for liquid scintillators are a high optical transmissivity at the optimal quantum efficiency of the photocathode, high light yield and a large Stokes shift between the absorption and emission spectra. The choice of the primary and secondary additives was made on the basis of shifting the emission spectrum into a region suitable for the response of the PMT. The greatest light yield was exhibited by

those samples in which the concentration of the primary and secondary additives were close to the point of saturation. To optimise the scintillator during manufacture, the primary and secondary additives were loaded past the point of maximum solubility at 60°C under nitrogen and during agitation. On cooling over a 24 h period self-seeding crystallisation occurred within the liquid. The scintillator was then centrifuged and filtered successively through a 20, 15 and 5 µm pore Buchner funnel.

Rapid addition of the loaded extractant to the liquid scintillator base was found to produce irreversible precipitation of the gadolinium compound. Instead blending was carried out using a titration column through which a carefully metered quantity of loaded extractant was added to the agitated base positioned in a flask on electronic scales. A second titration column filled with unloaded triethylphosphate was also incorporated within the apparatus so that additional amounts of extractant could be added should the miscibility of the loaded extractant with the base be poor. Care was taken to use only PTFE, glass or stainless-steel containers during the manufacture of the loaded scintillators.

Scintillators based on methylnaphthalene and α -hydroxytoluene were found to require less extractant to achieve 10% loading and therefore,

contained more active scintillator base than those based in diisopropylnaphthalene and phenylxylylethane. Fig. 1 shows the supersaturation dependence of gadolinium on each base of scintillator. The miscibility of the gadolinium-loaded extractant with phenylxylylethane was found to be very poor.

The light collection of each sample was measured using two 18 mm thick and 150 mm diameter muon telescope cells close coupled to two Electron Tubes 9390 PMTs. Each cell was mounted in optical contact with the window of its PMT. Since the refractive index of the perspex cell ($n \approx 1.51$) was similar to that of the glass window of the PMT, high light collection efficiency was expected. The light yield of each sample was measured at 20°C. Unloaded Eljen EJ399-01 (20% phenylxylylethane, 3 g/l PPO and 0.3 g/l POPOP in a mineral oil base) was placed in one cell while the other cell was used to test the range of scintillator liquids. The rate of muon coincidences between the cells was approximately 100 events/h and the mean peak position due to ionisation energy loss was approximately 3 MeV. Fig. 2 shows the effect of gadolinium loading on the light collection of each scintillator base. Increasing the loading of gadolinium required a higher percentage of triethylphosphate within the final blend. Since triethylphosphate has poor energy transfer

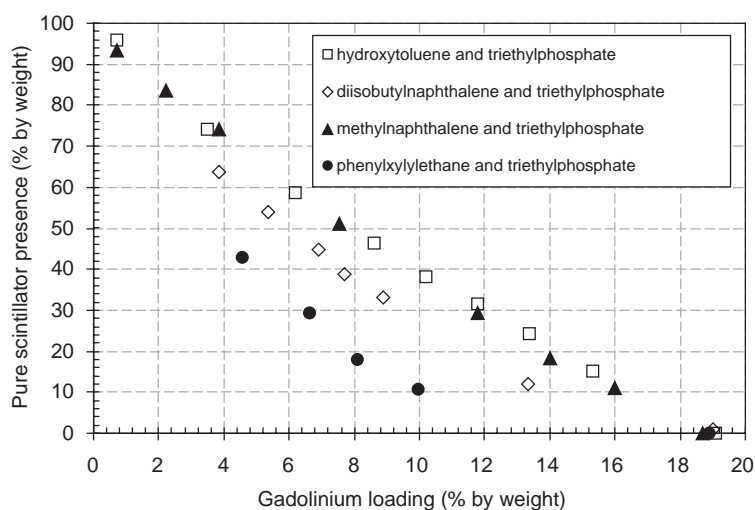


Fig. 1. Effect of increasing the gadolinium loading on the proportion of base scintillator within the blend.

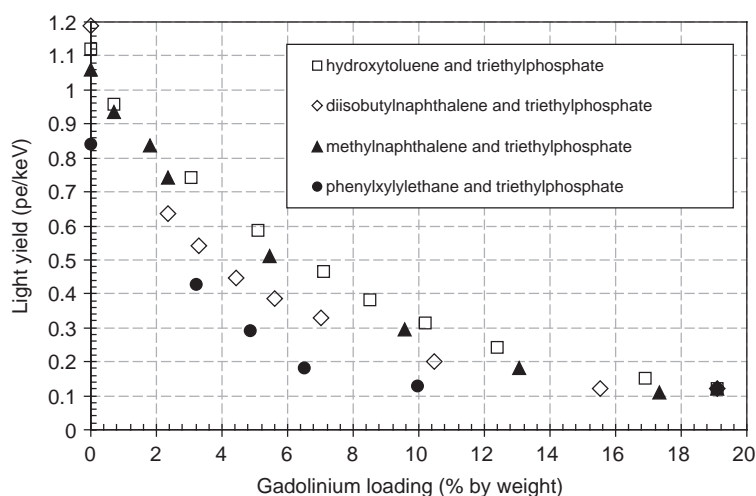


Fig. 2. Effect of increasing the gadolinium loading on the light collection from the scintillator blend.

properties, few molecules transfer their excitation energy to α -hydroxytoluene and phosphor molecules. The light yield diminished therefore due to the increased presence of gadolinium and also the reduced proportion of liquid scintillator within the mixture. Ten percent loaded gadolinium scintillators based in both methylnaphthalene and α -hydroxytoluene were found to retain approximately 30% of the scintillation yield of the unloaded scintillator.

The light yield and attenuation length within the detector must be maintained for a long period of time and the loaded scintillator must be stable. Unfortunately gadolinium nitrate is a strong oxidising agent capable of reacting with trace impurities within methylnaphthalene- and diisopropylnaphthalene-based scintillators with the effect that the liquid discolours turning yellow. This can be avoided by purifying the base scintillator prior to the addition of gadolinium but when dealing with tonne quantities, this level of purity would be difficult and costly to achieve and maintain. α -hydroxytoluene-based scintillators were therefore selected as offering the best compromise between long-term stability and light yield.

Pure α -hydroxytoluene-based scintillators were prepared containing a variety of compatible fluors and waveshifters selected to shift the emission

spectra to approximately 420 nm. Following addition of gadolinium and subsequent stability testing the optimum combination of fluor (2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole, $\lambda_{\text{emission}} = 362$ nm) and waveshifter (2-(1-naphthyl)-5-phenyloxazole, $\lambda_{\text{emission}} = 398$ nm) was selected.

The light collection efficiency of a solar neutrino detector is influenced not only by the light yield of the liquid scintillator but also by its transmissivity. The transmissivities of loaded and unloaded samples were measured with an Optronic 750 spectrophotometer. Collimated light from a tungsten source was passed through a quartz cell to a silicon detector. The pulse height produced was then measured from 200 to 650 nm. Cuvettes of identical cross-section but differing optical path length were compared, the difference in absorption used to calculate the attenuation length for that sample. The light output and the optical properties are strongly affected by the presence of dissolved oxygen and water, which can create contact compounds within the scintillator [18]. Deoxygenation was achieved by thoroughly flushing each sample with nitrogen for at least 30 min prior to recording measurements. The purified samples were then held under nitrogen in glass vials. The light collection, attenuation length and physical properties were evaluated and are shown in Table 1. A Labview DAQ was used to record

Table 1
Properties of gadolinium-loaded α -hydroxytoluene-based scintillators

Property	Percentage loading of gadolinium				
	0	2.5	5.0	7.5	10.0
Boiling point (°C)	205	205	207	208	212
Flash point (°C)	93	98	103	105	109
Light collection pe/keV	1.13 ± 0.057	0.78 ± 0.039	0.58 ± 0.029	0.46 ± 0.023	0.34 ± 0.017
Attenuation length (cm)	3010 ± 420	1460 ± 153	366 ± 18	209 ± 10	142 ± 8

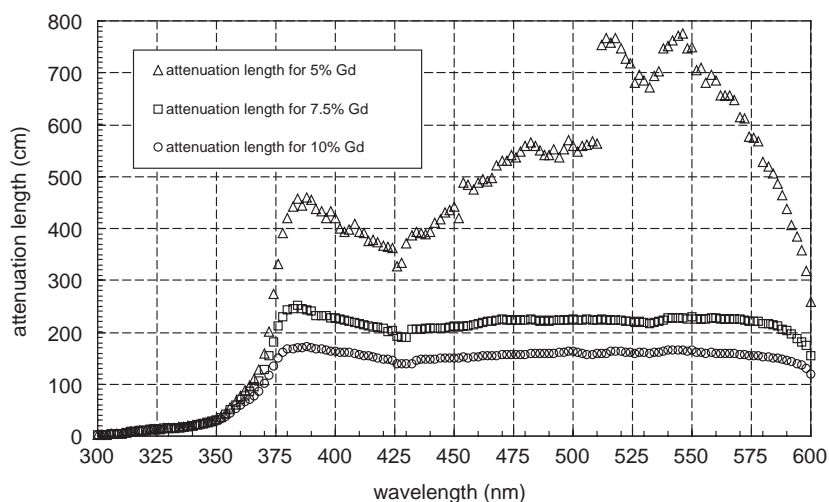


Fig. 3. Attenuation length of gadolinium-loaded α -hydroxytoluene-based liquid scintillator.

data over a 24 h period. The measured spectrum was then fitted to a Gaussian distribution, the error in the fit representing an error in the value of the light yield of no more than 5% for each measurement tabulated in Table 1 and Fig. 2. Fig. 3 displays attenuation length versus wavelength for several gadolinium loading fractions. Measurements of the attenuation length were taken by comparing each scintillator with a sample of distilled water of known transmissivity. The results were found to be very similar to those produced using variation of the path length. The measurement of each sample was repeated 20 times at 420 nm and the standard deviation given as the error in the mean value of those results. For a 10 wt% gadolinium loaded α -hydroxytoluene-based scintillator the attenuation length was found to be 142 ± 8 cm at 420 nm.

Both light yield and transmissivity are strongly affected by the proportion of solvent within the scintillator and the purity of the raw materials. Although increasing the proportion of solvent within the scintillator decreases its light yield, miscibility between liquids and particulate dissolution improves, thereby increasing the attenuation length and possibly increasing the net light collection for future large full size modules. During measurements of the attenuation length an improvement of 20% was achieved by adding a very small quantity of extractant for a 5% decrease in the light collection. The light yield of 10% loaded α -hydroxytoluene was found to remain constant on storage as shown in Fig. 4. The light attenuation length for the 10% gadolinium-loaded α -hydroxytoluene-based scintillator was measured on 27/4/02 using the Optronics 750

Spectrophotometer and found to be 1.42 ± 0.08 m at 420 nm. A measurement of the light attenuation length was made on 11/7/03. Its value was 1.45 ± 0.08 m at 420 nm indicating that the light attenuation length had not diminished over that time.

5. Conclusions

The result of this research has been the manufacture of a 10% loaded gadolinium scintillator with high light yield and transmissivity for use in solar neutrino detection and neutron measurements. We have described the properties, chemical composition and stability of the loaded scintillator and detailed processes required to ensure the manufacture of samples with high light collection and transmissivity. Because of its high-temperature stability, high-vapour ignition temperature and biological inactivity compared with commercially available gadolinium-loaded pseudocumene-based liquid scintillators, gadolinium-loaded scintillators based on α -hydroxytoluene have applications in large volume detectors of the future.

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