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# SOLVENT PURIFICATION AND FLUOR SELECTION FOR GADOLINIUM-LOADED LIQUID SCINTILLATORS

TIGISTI KESETE, AMANDA STORM, RICHARD L. HAHN, MINFANG YEH, AND SUZANNE SELEEM

## ABSTRACT

The last decade has seen huge progress in the study of neutrinos, elementary sub-atomic particles. Continued growth in the field of neutrino research depends strongly on the calculation of the neutrino mixing angle $\theta_{13}$, a fundamental neutrino parameter that is needed as an indicative guideline for proposed next-generation neutrino experiments. Experiments involving reactor antineutrinos are favored for the calculation of $\theta_{13}$ because their derivation equation for $\theta_{13}$ is relatively simple and unambiguous. A Gd-loaded liquid scintillator (Gd-LS) is the centerpiece of the $\bar{\nu}$ detector and it consists of ~99% aromatic solvent, ~0.1% Gd, and < 1% fluors. Key required characteristics of the Gd-LS are long-term chemical stability, high optical transparency, and high photon production by the scintillator. This summer's research focused on two important aspects of the $\bar{\nu}$ detector: (1) purification of two selected scintillation solvents, 1, 2, 4-trimethylbenzene (PC) and linear alkyl benzene (LAB), to improve the optical transparency and long-term chemical stability of the Gd-LS, and (2) investigation of the added fluors to optimize the photon production. Vacuum distillation and column separation were used to purify PC and LAB, respectively. Purification was monitored using UV-visible absorption spectra and verified in terms of decreased solvent absorption at 430nm. Absorption in PC at 430nm decreased by a factor slightly >10 while the absorption in LAB was lowered by a factor of ~5. Photon production for every possible combination of two solvents, four primary shifters, and two secondary shifters was determined by measuring the *Compton-Scattering* excitation induced by an external Cs-137 gamma source ($E_\gamma$ ~ 662-keV). The ideal shifter concentration was identified by measuring the photon production as a function of shifter quantity in a series of samples. Results indicate that 6g/L p-terphenyl with 150mg/L 1,4-Bis(2-methylstyryl)-benzene (bis-MSB) produces the maximum light yield for PC and 6g/L 2-(4-biphenylyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole with 50mg/L bis-MSB optimizes the light yield for LAB. Future work should focus on obtaining the fluorescence spectra for each of the shifters and studying the optical transparency of the LS as a function of shifter quantity.

## INTRODUCTION

Neutrinos ($\nu$) are neutral, nearly massless, subatomic particles. They pass through the surface of the Earth and all of its inhabitants at a rate of 65 billion particles per second per square centimeter. They exist as one of three flavors, electron, muon, and tau, but are capable of converting, or oscillating, between flavors [1]. Both neutrinos and antineutrinos ($\bar{\nu}$) are produced by beta-decay reactions; however, neutrinos are emitted from proton rich nuclei while antineutrinos come from neutron rich nuclei ($p \rightarrow \beta^+ + \nu + n$; $n \rightarrow \beta^- + \bar{\nu} + p$). The major sources of neutrinos include the Sun, nuclear reactors, and particle accelerators. The Sun produces electron neutrinos as a by-product of the overall fusion process ($4\ ^1H \rightarrow\ ^4He + 2\ e^+ + 2\ \nu_e$

+ 26MeV of energy), while nuclear reactors emit antineutrinos as part of the beta-decay of the fission products.

The last decade has seen huge progress in the study of neutrinos and their properties. Some major advancements include the confirmation of the theory of neutrino oscillation [3] and the experimental determination of two of the three neutrino mixing angles, $\theta_{12}$ and $\theta_{23}$. Continued growth in this field of research depends heavily on the measurement of the third mixing angle, $\theta_{13}$. As one of the fundamental neutrino parameters, $\theta_{13}$ is needed for future research, including experiments utilizing very long base-line accelerators to determine the mass of each of the neutrino flavors [1]. This knowledge could indicate whether neutrinos are part of the solution to the mystery of dark matter that is assumed to be holding the universe together.

Theta-13, $\theta_{13}$, can be calculated from experiments carried out at nuclear reactors or particle accelerator facilities. The nuclear reactor-based experiments, which measure the disappearance of antineutrinos, are favored because of their simpler derivation equation for $\theta_{13}$.

Metal-loaded liquid scintillators (M-LS), specifically those loaded with gadolinium (Gd), have been chosen as detectors for the reactor antineutrino experiment because of their high sensitivity [2]. In addition, the antineutrino interaction is detected via two coupled signals that produce a delayed coincidence in the LS. This suppresses a large number of uncorrelated background events. Due to the weakness of neutrino interaction, each of the several detectors will contain approximately 20 tons of Gd-LS scintillator, and have a total mass of around 100 tons.

The M-LS will consist of an aromatic solvent, both a primary and a secondary chemical shifter, and an organo-gadolinium complex. Antineutrino detection begins when an antineutrino collides with a proton, supplied by the organic solvent, releasing a positron and a neutron ($\bar{\nu}_e + p \rightarrow e^+ + n$). The positron instantaneously produces photons whose energies are indicative of the neutrino energy; in addition, two gamma rays of 511keV each are produced when the positron annihilates with a nearby electron. After a delay of ~30μs, a second emission of gamma-ray photons occurs from the thermalization of the neutron, which can occur by one of two mechanisms, $n + p \rightarrow D + \gamma(2.2MeV)$ or $n + Gd \rightarrow Gd^* \rightarrow Gd + \gamma$ (8MeV) [2]. The scintillation solvent molecules absorb the gamma photons, shift to their excited molecular states, and then re-emit the energy as ultraviolet light (~280nm). This energy is absorbed by the primary wavelength shifter or "fluor", which becomes excited and then re-emits the energy as photons with wavelengths in the 360nm region. Finally, the secondary wavelength shifter, which absorbs light in the 360nm range, will convert the energy to the visible blue light region (410nm-450nm) that is detected by the surrounding photomultiplier tubes (PMT). The signals from the PMT can then be amplified, converted to digital data by a multiple channel analyzer (MCA), and graphed. Collection of these data produces a Compton-scattering plot since the photons that reach the PMT have only a portion of the energy of the original gamma photon.

For the experiment to have the greatest effectiveness, the Gd-LS must have high photon yield, high optical transparency, and long-term chemical stability [2]. Detection of an antineutrino interaction depends on the scintillation efficiency of the detector in converting the produced gamma photons into detectable light in the blue region, thus a scintillator with a high light yield is vital for a sensitive detector.

High optical transparency is necessary because the detector vessels will be very large, several meters in diameter, and photons must reach the PMT's on the outside of the detector. The scintillation solution should interfere as little as possible with light passage so the solvents must be exceptionally pure. The other motivation for extensive purification is to eliminate impurities that could react within the liquid scintillator and cause it to degrade. At a minimum, the reactor antineutrino experiment must run for 3 years. Radioactive contaminants also present an additional problem since some can mimic the neutron-capture signal of an antineutrino interaction, giving false results.

The research presented here focused on optimizing two of the key LS characteristics, solvent purity and high photon yield. Two selected scintillation solvents, 1, 2, 4-trimethylbenzene (pseudocumene - PC) and linear alkyl benzene (LAB), were purified to improve the optical transparency and long-term chemical stability of the Gd-LS. Photon yields were measured and compared for scintillation solutions that varied in the combinations and concentrations of the added wavelength shifters to find which solution had the maximum photon production. Four primary shifters, p-terphenyl (p-TP), 2-(4-Biphenylyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (butyl-PBD), 2,5-diphenyloxazole (PPO), and 2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD), and two secondary shifters, 1,4-bis(2-methylstyryl)-benzene (bis-MSB) and 1,4-bis(4-methyl-5phenyloxazol-2-phenyl)benzene (POPOP), were used.

## MATERIALS AND METHODS

All chemical shifters were used as received and, with the exception of PPO (Fluka), were made by Sigma-Aldrich. The two scintillation solvents, PC (Aldrich) and LAB (Petresa), were further purified using vacuum distillation and dry column separation, respectively. With the vacuum distillation, both the first ~20mL of distillate and the last ~30mL of residue were discarded as waste. The extent of the purification was monitored by the comparison of UV-visible absorbance spectra taken before and after purification. Spectral data were collected and analyzed with a Shimadzu UV-1601 UV-Visible Spectrophotometer using air as the reference material. In the case of PC purification, a UV-visible spectrum of the final residue was also obtained. When analyzing the UV spectra, a significant decrease in solvent absorption within the wavelength region of 430nm was used to indicate an increase in purity level.

A list of all the scintillation solutions tested is given in Table 1. For the initial photon yield measurements, all the LS solutions were made using 10.0g of solvent, 0.030g of primary shifter, and 0.0015g of secondary shifter. A series of samples were then made to measure the photon yield (S%) of two specific shifter combinations, LAB + butyl-PBD + bis-MSB and PC + p-TP + bis-MSB, at different shifter concentrations in order to find the lowest concentration that produced the greatest amount of light. The primary shifter concentration was set at 6g/L for both butyl-PBD and p-TP while the secondary shifter, bis-MSB, was added at concentrations of 10, 20, 50, 100, 150, and 500mg/L.

| Fluors | s% | Δs% |
|---|---|---|
| LAB+PPO | 1862.50 | 40.31 |
| LAB+BU | 1935.50 | 55.86 |
| PC+PPO | 2115.60 | 57.12 |
| PC+PBD | 2172.00 | 66.30 |
| PC+BU | 1911.50 | 62.04 |
| PC+pTP | 1317.67 | 44.16 |
| LAB+PPO+MSB | 2332.00 | 59.43 |
| LAB+PPO+POPOP | 2155.00 | 91.65 |
| LAB+BU+POPOP | 2388.00 | 73.98 |
| LAB+BU+MSB | 2287.50 | 6.36 |
| PC+PPO+MSB | 2475.57 | 66.54 |
| PC+PPO+POPOP | 2208.00 | 79.27 |
| PC+pTP+MSB | 2921.25 | 50.76 |
| PC+pTP+POPOP | 2753.67 | 46.05 |
| PC+PBD+MSB | 2597.00 | 2.83 |
| PC+PBD+POPOP | 2693.50 | 6.36 |
| PC+BU+MSB | 2378.50 | 79.90 |

**Table 1.** Average LS Light Yields.

The setup for the LS light yield measurement consisted of a 10 µCi, sealed Cs-137 gamma source, a Hamamatsu R2154-02 Photomultiplier tube, and a EG&G ORTEC 572 amplifier. Each sample was placed on top of the PMT and externally radiated with the Cs-137 source. Signals produced by the PMT were amplified to 5V and then digitally converted and collected by a multiple channel analyzer (MCA) and Genie2000 software. The data were reconstructed as Compton-scattering curves using Microsoft Excel and analyzed by the Full Width Half Maximum (FWHM) method to obtain the photon production value.

## RESULTS

Figure 1 compares the UV-visible absorbance spectra of LAB before and after purification. The same comparison is shown for PC in Figure 2 along with the spectrum of the residual distillation fraction. In both Figures there is a notable decrease in absorbance, especially in the 350-450nm region. As a result of purification, the absorbance at 430nm decreases by a factor of ~5 for LAB and ~10 for PC. LAB's improvement factor is smaller because it arrives from the company in a purer state.

Table 2 describes the solubility of the six shifters in each of the solvents. Ease of solubility for primary shifters in PC is PPO>butyl-PBD>PBD>p-TP and for secondary shifters is bis-MSB>POPOP. Because LAB is a less effective solvent, the shifters either take longer to dissolve or are unable to dissolve completely. The order of solubility for primary shifters in LAB is PPO>butyl-PBD and for secondary shifters is bis-MSB>POPOP. Both PBD and p-TP were insoluble in LAB.

Light yield measurements were taken three times or more for each solvent-shifter combination. The average light yield values along with their respective standard deviations are given in Table 1. The addition of a secondary shifter increased the light yield in all

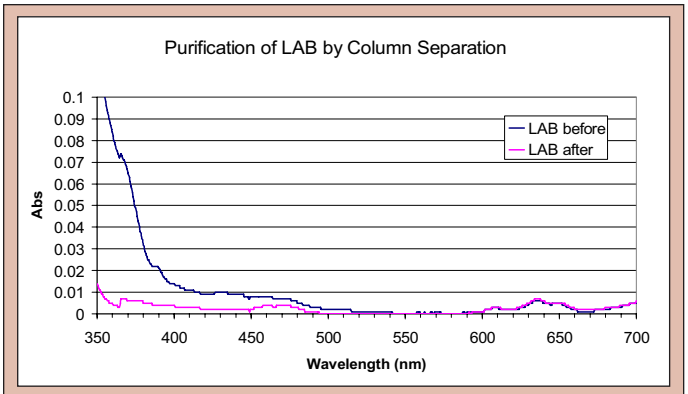


**Figure 1.** UV-visible spectra of LAB before and after purification.

| Shifters | In PC | In LAB | Comments |
|---|---|---|---|
| butyl-PBD (Primary) | Soluble | Soluble | Dissolved quickly in PC, Overnight in LAB |
| PPO (Primary) | Soluble | Soluble | Dissolved quickly in PC, Overnight in LAB |
| PBD (Primary) | Soluble | Insoluble | Dissolved in PC after a period of shaking |
| p-TP (Primary) | Soluble | Insoluble | Dissolved in PC after a period of shaking |
| bis-MSB (Secondary) | Soluble | Soluble | Dissolved more quickly in PC than LAB; both required shaking |
| POPOP (Secondary) | Soluble | Soluble | Slower to dissolve than MSB, required vigorous shaking for PC and LAB |

**Table 2.** Wavelength-Shifter Solubility Data.

the scintillator samples by at least ~10% with the largest increase resulting from the addition of bis-MSB to PC and p-TP (from 1317 to 2921 S%). The LS with the highest photon production for each solvent was PC + p-TP + bis-MSB and LAB + butyl-PBD + POPOP.

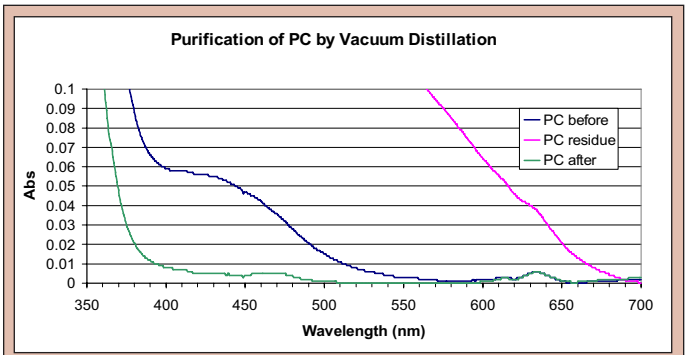


**Figure 2.** UV-visible spectra of PC before and after purification plus residue fraction.

Figure 3 shows the Compton-Scattering spectra of selected LS. These spectra were used to derive the scintillators' light yields. The x-axis in these Figures is directly proportional to photon production so the longer the data plot the greater the light yield.

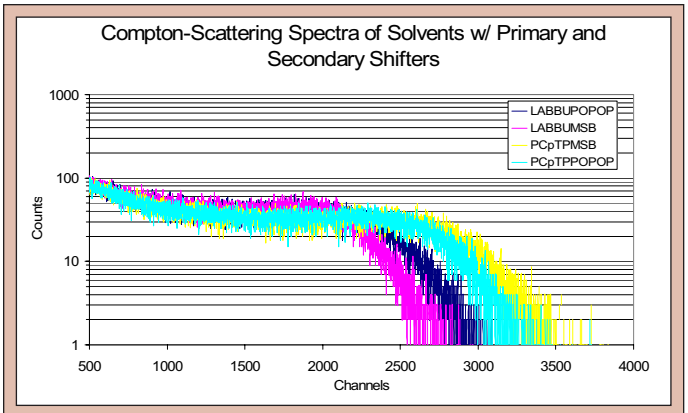


**Figure 3.** Compton-Scattering spectra of selected LS.

Figures 4 and 5 display light yield as a function of bis-MSB concentration for two LS, PC + p-TP + bis-MSB and LAB + butyl-PBD + bis-MSB, respectively. Light yield roughly increases with concentration up to a point and then levels off. Both tested LS begin leveling off in light yield at a concentration of ~150mg/L bis-MSB.

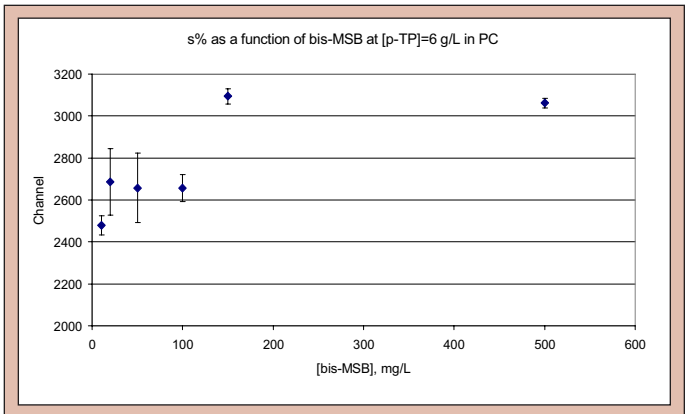


**Figure 4.** Light yield as a function of bis-MSB concentration in PC.

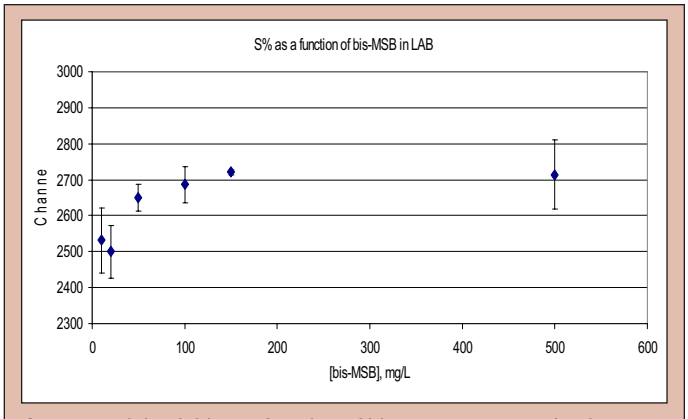


**Figure 5.** Light yield as a function of bis-MSB concentration in LAB.

## DISCUSSION AND CONCLUSIONS

Results from the purification of PC and LAB show that their respective purification techniques, vacuum distillation and dry column separation, were effective at eliminating many impurities that were absorbing visible light. The evidence for this is that the visible light absorption in both solvents decreased by a factor of 5 or more after purification. Reducing the level of these contaminants not only rids the solution of foreign chemicals that could cause the LS to degrade but it also increases the scintillator's attenuation length by reducing the re-absorption of the scintillation light.

From the data gathered it has been determined that 6g/L p-TP with 150mg/L bis-MSB is the best shifter combination for PC while 6g/L butyl-PBD with 50mg/L bis-MSB is the best combination for LAB. The primary consideration for these choices was optimization of light yield but shifter solubility and cost were also taken into account.

Shifter solubility is an important consideration because the final Gd-LS for anti-neutrino experiment must be carried out on a very large scale (~200 tons of LS). Using a shifter that is difficult to dissolve would not be an economical use of time or of money.

In an experiment that is estimated to cost over 60 million dollars, it is important to save money wherever practically possible. One of the greatest expenses for the reactor antineutrino experiment is expected to be the purchase of fluors. As a result, the ideal shifter quantity should show a reasonable increase in light yield for every increase in concentration.

The LS containing p-TP and bis-MSB in PC had the highest average photon production out of all the samples tested. Since PC is such an effective solvent, consideration of shifter solubility does not come into play. There is also no contesting the ideal bis-MSB concentration since there is a large difference (>20%) in light yield between the samples with 100mg/L and 150mg/L bis-MSB.

Including experimental uncertainties, LAB had three shifter combinations with very similar light yields. Out of the three, butyl-PBD with bis-MSB was chosen because its average had the greatest precision and bis-MSB is easier to dissolve than POPOP. The concentration of 50mg/L bis-MSB is considered the optimal quantity for the LAB. Although 150mg/L produces more photons, its light yield is only 3% greater than the 50mg/L sample and requires three times more shifter.

Future work should focus on determining why these two solvent-shifter combinations produce more light than others. This can be accomplished by measuring the fluorescence spectra for each of the shifters and both LS. A scintillator's photon production, in addition to its quantum efficiency, depends on the extent to which the solvent's emission spectrum overlaps the primary shifter's absorbance spectrum and likewise on the overlap of the primary shifter's emission spectrum with the secondary shifter's absorbance spectrum. Greater overlap increases light transfer efficiency and the photon yield.

## ACKNOWLEDGMENTS

We would like to thank our mentors, Dr. Richard Hahn and Dr. Minfang Yeh for all the time they invested in introducing us to this field of study as well as guiding us through our research. Our thanks go to the U.S. Department of Energy, Office of Science for making this program available. We are thankful to Dr. Sri and Central State University for funding our research though the NSF-sponsored Quest program. We appreciate the hospitality of Brookhaven National Laboratory, especially the Chemistry Department, for providing the facilities needed for this internship. Finally, we are thankful to the Office of Educational Programs for managing and maintaining this wonderful undergraduate research program.

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