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Radiopure Metal-Loaded Liquid Scintillator

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Radiopure Metal-Loaded Liquid Scintillator

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Abstract. Metal-loaded liquid scintillator plays a key role in particle and nuclear physics experiments. The applications of metal ions in various neutrino experiments and the purification methods for different scintillator components are discussed in this paper.

INTRODUCTION

Liquid scintillator (LS) for neutrino research is growing over decades of studies since the early discovery experiment of Reines and Cowan[1-4]. Furthermore, the development of next-generation scintillator detectors is currently in great demand for a variety of future frontier experiments, including double beta decay[5-6], reactor antineutrino[7-8], neutrino beam physics[9-10], safeguard[11], and Dark Matter search[12]. A summary of metal-doped scintillator detector (M-LS) in application for particle and nuclear physic experiments is presented in Figure 1.

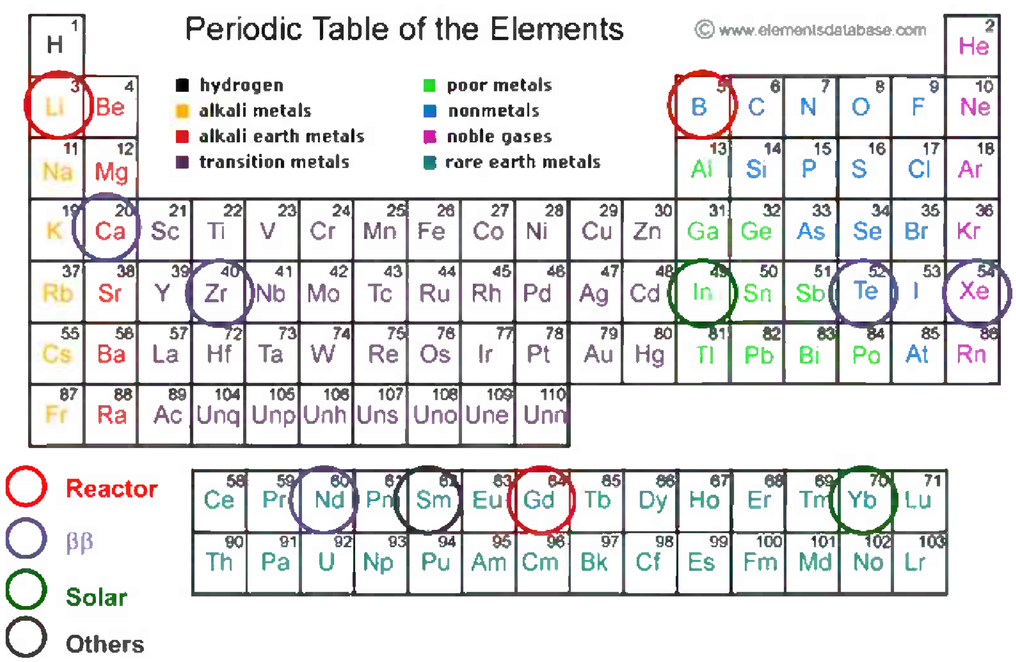

FIGURE 1. Metal-loaded liquid scintillator for neutrino researches

Chemically, it is not trivial to synthesize an organometallic complex to be soluble in organic scintillator, which is a non-polar aromatic compound (i.e. containing phenyl groups and primarily C and H) that is generally immiscible with aqueous solutions. Until the recent breakthrough of doping aqueous isotopes directly using water-based liquid scintillator developed at Brookhaven National Laboratory[13], loading of metallic ion into organic scintillator cannot be achieved without the aid of a complexing ligand that forms an organometallic complex to be extracted in organic solvent. Much of this organometallic chemistry has already been developed in the fields of separation chemistry and chemical treatment in the nuclear fuel cycle. Several organic complexing agents, for example (i) carboxylic acids that can be neutralized with inorganic bases, such as NH_4OH, to form carboxylates of metal ions, (ii) organic phosphorus-oxygen compounds (RPO), such as organic phosphates or phosphine oxides, that can complex neutral inorganic species, and (iii) organic diketones, such as acetyl acetonate, used in the synthesis of M-LS have been identified for reactor antineutrino experiments.

Key aspects of metal-loaded liquid scintillator for neutrino detection are (a) long-term chemical stability, (b) high optical transparency, (c) high photon production, and (d) ultra-low impurity content, mainly of natural radioactive contaminants, such as uranium, thorium, radium, and radon. Being able to satisfy these requirements depends on R&D in chemistry and nuclear chemistry. We have optimized these procedures, with regard to the key aspects listed above[14]. The chemical purification and physical performance of M-LS are described in this paper, focusing on (i) establishing the chemical procedure that is capable of removing lanthanides and actinides impurities from inorganic compounds, (ii) selecting a scintillator solvent that has good optical property with high photon efficiency and is feasible for large quantity purification and production, and (iii) optimizing and cleansing fluor and wavelength shifter associated with scintillator.

PURIFICATION METHODS

A variety of liquid scintillators, linear alkyl benzene (LAB), pseudocumene (PC), di-isopropylnapthalene (DIN), phenylxylylethane (PXE), and phenylcyclohexane (PCH), has been identified as the detection mediums for various neutrino detectors. The developed purification techniques are divided into two categories: the removal of *chemical* and of *radioactive* impurities. The levels of non-radioactive chemical species that can adversely affect the optical properties of the scintillator have to be strictly controlled. Indeed, the removal of chemical impurities not only can increase the transmission of light in the LS, but can also enhance the long-term stability of metal-doped scintillator. Our investigations found that some impurities could induce slow chemical reactions that would cause the transparency of M-LS to deteriorate gradually.

Different procedures have to be used for inorganic species (often prepared in water) and other starting aqueous solutions (i.e. ammonium hydroxide for pH adjustments), which could contain naturally occurring radioactive impurities, such as Th^{4+}, U^{4+} and U^{6+} (as UO_2^{2+}). Purification steps have to be developed to reduce these radioactive species to the desired concentration level, depending on the requirements of the experiments. Two purification methods, cation exchange and solvent extraction, are often considered, but the latter technique is preferred, for aqueous solutions. Several organic ligands, such as tributylphosphine (TBP), trioctylphosphine oxide (TOPO), tetradecylthioacetic acid (TTA), and triphenylphosphine oxide (TBPO), have been developed from the nuclear industry for such applications. In the following sub-sections, few purification methods, focusing only on the non-aqueous components, but including the inorganic species, of M-LS, are described.

Vacuum Distillation

The high-volatility liquids, such as the carboxylic acids and PC, can be purified by temperature-dependent, vacuum distillation, using a 30-cm long distillation column filled with Teflon coils and a mechanical rotary vacuum pump to keep the system pressure <0.04 bar. The glass distillation column is composed of many theoretical plates that can effectively separate the organic solvents, which have different boiling points, at ~10°C intervals. The vacuum distillation procedure is set to finish when ~90% of the distilled solvent was collected. The ~10% of the higher boiling-point fraction remaining in the distillation flask usually has a darker color, indicating that the distillation process has successfully separated the colored impurities in the original solvents (as received from the vendors). The purity of trimethylhexanoic acid (TMHA) before and after purification is illustrated in Figure 2. The data show that the optical transparency of the solvent is improved significantly by purification procedure. In addition, the vacuum distillation also removes most radioisotopic impurities at >95% efficiency.

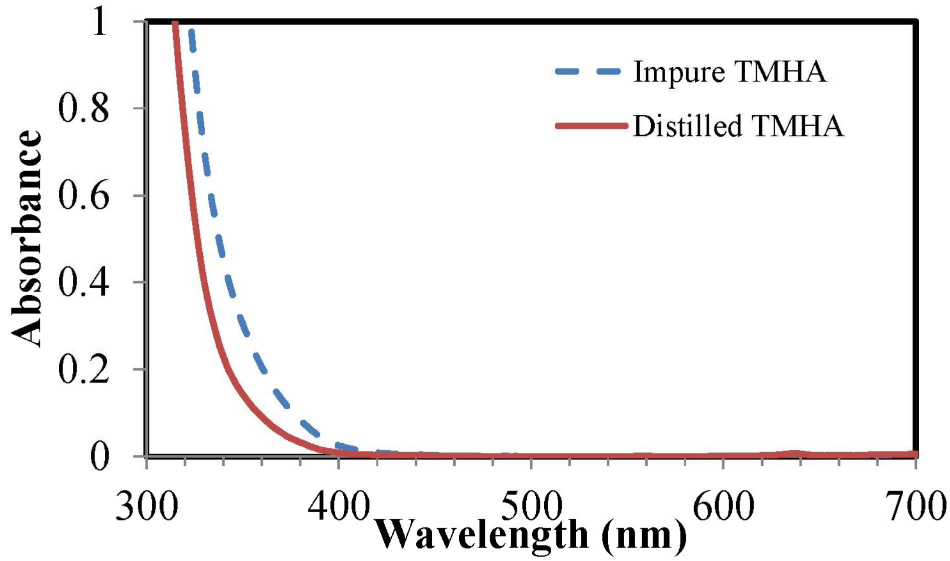

FIGURE 2. Improvement of optical transparency of complexing ligand, TMAH, by vacuum distillation

Column Separation

Column Separation is very effective to remove impurities from liquid scintillator with regard to its optical clarity. Figure 3 presents the optical improvements of low-volatility liquid scintillators, LAB and DIN, purified by dry column absorption (50-cm long glass column loaded with activated neutral Al_2O_3 of 150 mesh, ~58Å particle size). Such separation columns also act as filters for targeting radioactive isotopes, such as cobalt and iron generated from cosmogenic activation. However the efficiency of removing these metallic impurities has not yet been proven to be consistent, largely due to column-geometry effect.

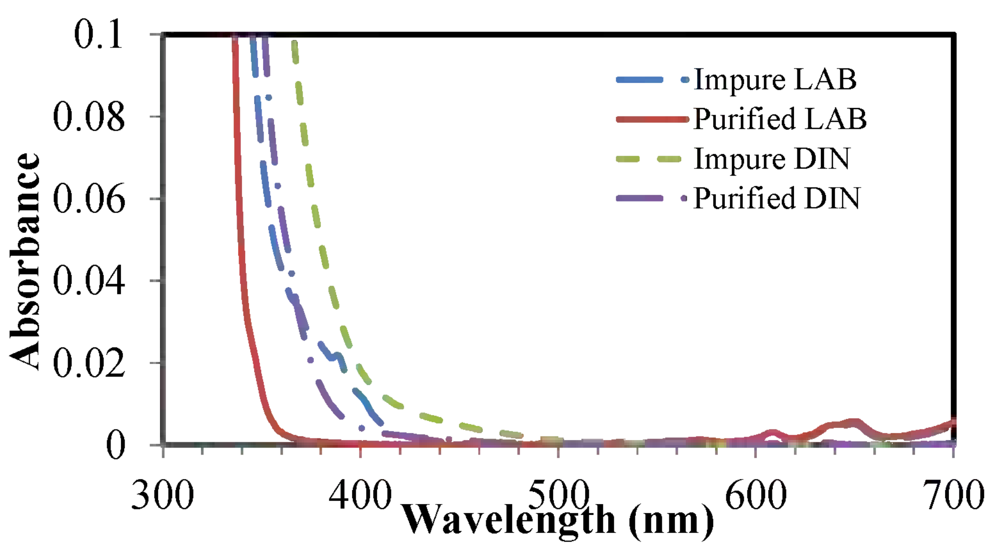

FIGURE 3. Removal of colored impurities of LAB and DIN by column separation

Recrystallization

Recrystallization is the most used method to purify either solid organic or inorganic metallic compounds. By dissolving the starting material in an appropriate solvent, either the desired compound or impurities can be coaxed out of solution, leaving the other behind. Figure 4 shows purification of telluric acid by chemical recrystallization[15]. The impure raw material was first dissolved in water and then precipitated out by the addition of nitric acid. The cobalt from the spiked telluric compounds was removed by a factor of $>10^2$. An alternative purification can also be achieved by a temperature-controlled, thermal recrystallization using a hot solvent, followed by slowly cooling down the solution to grow a pure crystal lattice. However the efficiency of thermal recrystallization is not as high as that of chemical recrystallization.

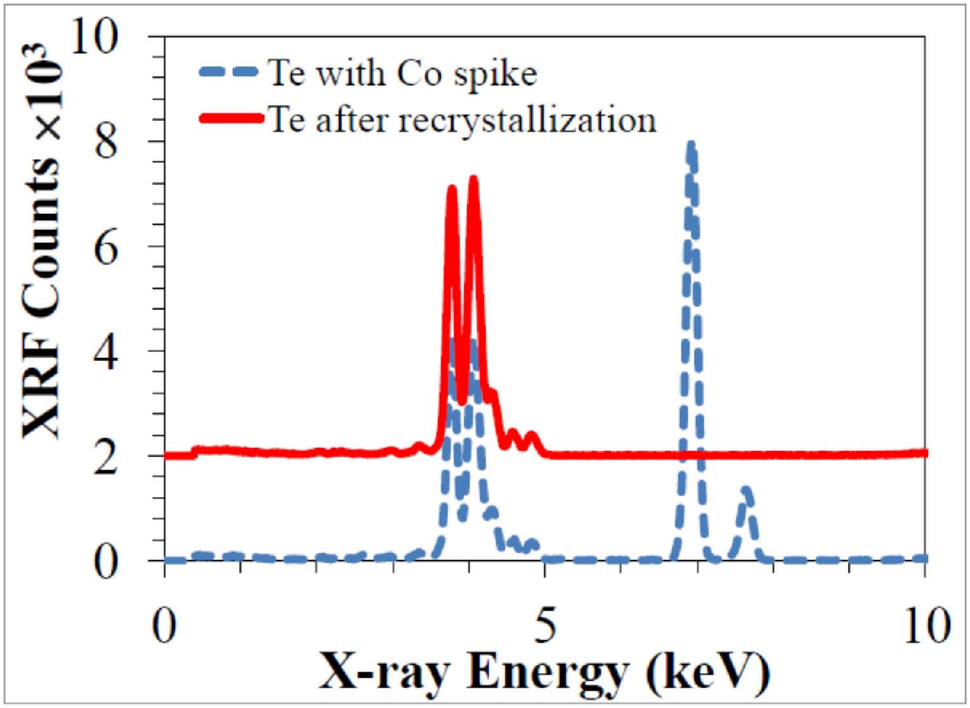

FIGURE 4. Cobalt removal from telluric acid by chemical recrystallization

Self-Scavenging

Scavenging is another technique to remove trace amounts of a radioelement by co-precipitating it with a macro amount of a chemically similar stable element. However, the use of iron or some other conventional scavenging agents might have negative effects on the chemical stability or optical transparency of the liquid scintillator. Thorium is extensively hydrolyzed even in acidic solutions, the reaction proceeding stepwise via intermediates, such as $Th(OH)_3^+$. Values of solubility product from -37.9 to -47.3 have been reported for the reaction $Th(OH)_4 \rightarrow Th^{4+} + 4OH^-$. Since K_{sp} for most inorganic metallic compounds in water is many orders of magnitudes greater than that for Th, there should be a pH range where a separation of Th and other metallic ions could be effected. A simple process consisting of a pH controlled partial hydrolysis and filtration ("self-scavenging") would remove thorium and possibly other contaminants. Figure 5 shows close to 100% efficiency of removing Th from Gd in a solution of pH 6 or higher[16]. This self-scavenging method could also be beneficial in industrial-scale lanthanide production.

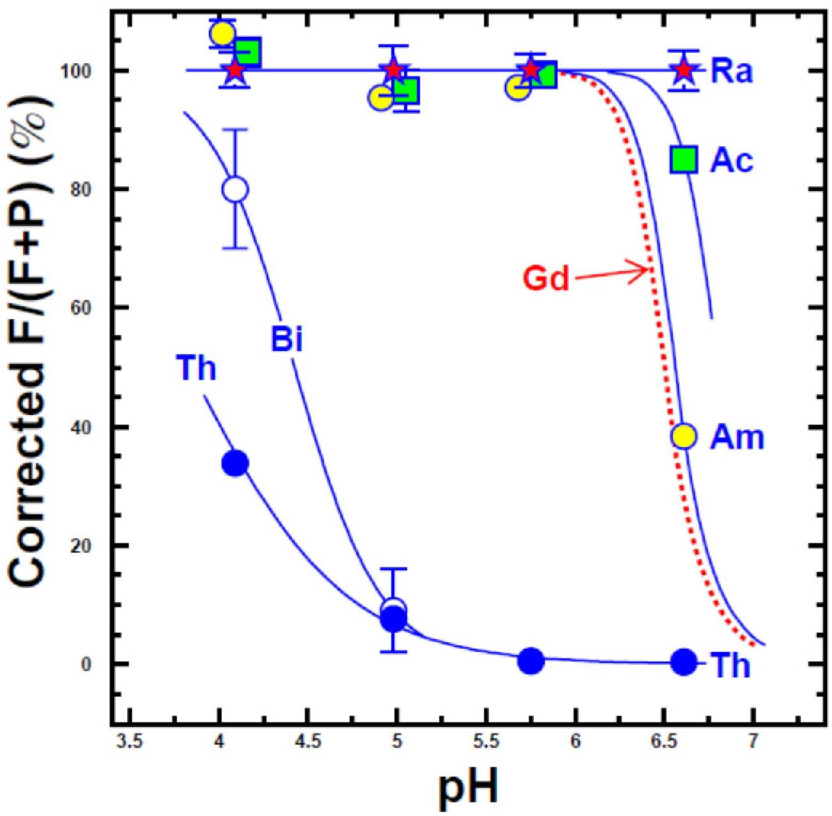

FIGURE 5. Removal efficiency of thorium from gadolinium as a function of pH

CONCLUSIONS

The qualities and impurities of starting materials, including inorganic species, liquid scintillator, mixing ligands, fluor and shifter, for the production of M-LS could vary with different vendors even at the same quoted purity level. Thus the properties of M-LS, such as metal-loading capability, chemical stability, photon production yield, and optical property, will change from one vendor to another and even from one production batch to another. The purification is essential to ensure the excellence of metal-doped liquid scintillator and thus provides a direct control of physical performance of neutrino detector.

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