# Extraction Methods in Development of Gd-Loaded Liquid Organic Scintillators for Antineutrino Detection: 2. Scintillators Based on Solutions of Gadolinium 2-Methylvalerate

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**Abstract**—Complexes of Gd with carboxylic acids  $C_4$ – $C_9$  were prepared, and their properties were studied: solubility in water and organic solvents in relation to temperature, melting points, and decomposition points. A procedure was developed for removing water from gadolinium 2-methylvalerate Gd(2MVA)<sub>3</sub> to a final content not exceeding 0.01%. To increase the solubility of Gd(2MVA)<sub>3</sub> in low-polarity organic solvents and to stabilize the resulting organic solutions, it was suggested to add extractants such as 2-methylvaleric acid (H2MVA) or neutral organophosphorus compounds: triisoamylphosphine oxide (TIAPO) or trioctylphosphine oxide (TOPO). Liquid Gd-loaded organic scintillators based on Gd(2MVA)<sub>3</sub> solutions with additions of H2MVA, TIAPO, and TOPO in trimethylbenzene (TMB), phenylxylylethane (PXE), and their mixtures with dodecane were prepared. Long-term tests (up to 2 years) of the stability of the optical properties of the scintillators obtained proved their stability at temperatures of up to 30°C. At elevated temperatures (40°C and higher), the scintillators degrade. The previously made suggestion that water in the scintillator negatively affects its optical properties in prolonged storage was confirmed.

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Long-term and large-scale experiments in neutrino physics became the next step in studying the basic properties of neutrino. The discovery of neutrino oscillations, i.e., transition of one type of neutrino into another, made it necessary to go beyond the framework of the standard theory of electrically weak interactions and admit nonzero mass of neutrino. The most important studies in the field of neutrino physics shifted toward determination of neutrino mass and its mixing angles (probabilities of transition of one type of neutrino into another). Reactor installations are powerful sources of low-energy electronic antineutrino (fluxes  $\sim 10^{13}$  v cm<sup>-2</sup> s<sup>-1</sup> near the biological shield surface), which allows their use as a convenient tool for neutrino research. Another important aspect of neutrino physics is associated with studying astrophysical objects, e.g., supernova outbursts. A supernova outburst occurring as a result of star collapse is also a source of short-term powerful neutrino radiation. Recording of these rare events and measurement of their spectral characteristics bear important information both on the nature of a supernova outburst and on the neutrino properties. As the interaction of neutrino with the target substance is weak, one of the major requirements to such experiments is the development of largetonnage detectors. The most widely used today are detectors based on hydrogen-containing liquid organic scintillators (LOSs) in which antineutrino reacts with proton:  $v_e + p \rightarrow e^+ + n$ . The energy of reaction particles, lost as a result of ionization, is transferred to dissolved scintillation additives (PPO). Their deexcitation is recorded by photoelectron multipliers. The technique of delayed coincidence from two events caused by instantaneous signal from positron and delayed by ~180  $\mu$ s  $\gamma$ -quantum (2.2 MeV) from the capture of thermalized neutron on hydrogen allow identification of the neutrino interaction. To improve the characteristics of a scintillator as a detector for neutrino detection,

Gd-loaded scintillators are used. Introduction of Gd to an LOS allows the neutron lifetime in the scintillator (the neutron capture cross section of the natural mixture of Gd isotopes is higher by approximately 5 orders of magnitude than that of hydrogen) to be decreased to 30 µs at 0.1% concentration of Gd. In addition, it is significant that the total energy release of the  $\gamma$ -quanta in the neutron capture by the <sup>155</sup>Gd and <sup>157</sup>Gd nuclei is ~8 MeV, which considerably exceeds the natural surrounding radioactive background (2.6 MeV, <sup>208</sup>Tl). Both these factors allow the background to be substantially suppressed and hence the neutrino detection efficiency to be increased.

As the Gd concentration in the scintillator is low, its effect on the detector characteristics (light output, transparency) is acceptable.

The problem of transferring metals into an organic phase to obtain stable solutions is similar to problems that are solved in the development of various extraction processes. Therefore, in our previous studies we examined extraction systems suitable for preparing Yb-, In-, and Gd-loaded scintillators for neutrino detection [1–4]. The main components of a metal-loaded LOS should be a metal-containing additive, a hydrogen-containing organic liquid with the maximum possible H : C ratio, and a scintillation additive. As a metal-containing additive we suggested extractable metal complexes with carboxylic acids [1, 3, 4]. As experiments with neutrino are long-term, the main requirement to a scintillator is its chemical stability and stability of its optical properties (transparence and light output) for a long period (three years and more), because a decrease in the transparence or quantum efficiency (light output) increases the experimental error. The scintillator stability implies that the total amount of light collected on the photodetector should be constant. The major possible causes of a decrease in the light output are a decrease in the scintillation efficiency of molecules containing aromatic rings and formation of new "quenching" molecules, which leads to a decrease in the efficiency of excitation transfer between molecules; a decrease in the solution transparence in the range of the emission spectrum due to formation of new compounds having absorption bands in this range; precipitation of metal compounds due to hydrolysis and polymerization.

Gd-loaded LOSs with the Gd concentration of 1 g  $l^{-1}$  have been used for detecting thermal neutrons [5] and for recording reactor antineutrino in Palo Verde [6] and CHOOZ [7] experiments. In all the cases, the scin-

tillators rapidly lost transparence (by a factor of  $\sim 2$  in 6 months), which did not meet the experimental requirements.

It was shown in our previous studies [1, 3, 4] that the metal-loaded organic phase prepared by traditional liquid extraction inevitably contained water and the use of available desiccants did not ensure complete dehydration but contaminated the scintillator with undesirable desiccant components. It was also noted that a decrease in the water content of the organic phase led to an increase in the scintillator stability. Therefore, we concluded that it would be appropriate to isolate gadolinium carboxylates from their extracts, examine the possibility of their dehydration using methods that do not contaminate the target product with foreign substances, and subsequently prepare the scintillator by dissolving anhydrous gadolinium carboxylate in organic solvents.

The goal of this study was to prepare liquid organic Gd-containing scintillators for detection of reactor antineutrino, with the Gd concentration [Gd](o) = 0.85-1 g l<sup>-1</sup>, stable for 3 years and more.

# EXPERIMENTAL

In our study we used an aqueous solution of gadolinium chloride, prepared by dissolving Gd<sub>2</sub>O<sub>3</sub> (99.99%) pure) in hydrochloric acid (ultrapure grade). Carboxvlic acids (isobutanoic, HiBA; hexanoic, HHexA; 2-ethvlbutanoic, H2EtBuA; 2-methylvaleric, H2MVA; isovaleric, HiVA; heptanoic, HHepA; 2-ethylhexanoic, H2EtHexA) (Aldrich, initial purity 98-99.5%, transparence 1.6-9.0 m) were purified by double vacuum distillation, after which their transparence was 12-15 m. In our study we used organic solvents: 1,2,4-trimethylbenzene (Enichem), dodecane and light white mineral oil (Aldrich), and phenyl-o-xylylethane (Koch Chemical Company). The solvents were purified by passing through columns packed with Al<sub>2</sub>O<sub>3</sub>, after which their transparence was no less than 10-15 m. The Gd concentration in the aqueous and organic phases was determined by complexometric titration (EDTA) with Xylenol Orange indicator [8], and also by  $\gamma$ -counting of <sup>159</sup>Gd.

The water content of the organic phase was determined by Fischer titration with a Titroline KF titrator. The transparence of scintillator samples ( $L^{430}$ ) was determined at 430 nm using a UV/VIS Perkin–Elmer Lambda 18 spectrophotometer in cylindrical quartz cells with a length of 100 mm.  $L_{\lambda i}^{\text{att}}$  was determined as the distance at which the light intensity decreased by a factor of 1/e using the formula  $L_{\lambda i}^{\text{att}} = d/A_{\lambda i} \ln 10$ , where d is the optical length of the measured sample, i.e., the length of the quartz cell, and  $A_{\lambda i} = A_{430 \text{ nm}} - A_{\text{min}}$ , i.e., the light absorption at the required wavelength (430 nm) relative to the absorption minimum in the range 450–600 nm. The light output of the samples was determined by the standard procedure: comparison of the amplitude spectra of the samples upon their irradiation with a  $\gamma$ -ray source (<sup>137</sup>Cs) with those of the reference under the same geometric conditions with the same  $\gamma$ -ray source.

The IR spectra of gadolinium carboxylate samples were recorded on a Nexus IR Fourier spectrometer (Nicolet) in the range  $4000-400 \text{ cm}^{-1}$ .

The TGA diagrams were obtained with a Perkin– Elmer Pypis 1 TGA derivatograph.

When examining the compatibility of scintillators with the structural material of the detector, we used Acryl GS-233 organic glass (Rhome).

As scintillation additives we used 2-(4-biphenyl)-5phenyloxazole (BPO), 2,5-diphenyloxazole (PPO), and *p*-bis(*o*-methylstyryl)benzene (BisMSB). The range of maximal sensitivity of photoelectron multipliers used in this study was 380–450 nm.

# **RESULTS AND DISCUSSION**

# Preparation of Gadolinium Carboxylates with the Minimal Water Content and Study of Their Properties

A study of Gd extraction with carboxylic acids (CAs) showed that, depending on pH of the equilibrium aqueous phase, complexes of various compositions can be present in the organic phase: GdR<sub>3</sub>· 3HR·*n*H<sub>2</sub>O and GdR<sub>3</sub>·*n*H<sub>2</sub>O, where n = 1-2, HR is a carboxylic acid, and R<sup>-</sup> is its anion. An increase in pH of the equilibrium aqueous phase over 8.5 led to the formation of gadolinium hydroxycarboxylates Gd(OH)<sub>x</sub> R<sub>3-x</sub>·*n*H<sub>2</sub>O. It was found that complexes GdR<sub>3</sub>·3HR·*n*H<sub>2</sub>O are readily soluble in low-polarity organic solvents, and the complexes GdR<sub>3</sub>·*n*H<sub>2</sub>O and Gd(OH)<sub>x</sub>R<sub>3-x</sub>·*n*H<sub>2</sub>O are poorly soluble.

We failed to completely dehydrate Gd extracts with available desiccants [1]. Therefore, we decided to iso-

late gadolinium carboxylates in the form  $GdR_3 \cdot nH_2O$ , difficultly soluble in organic solvents, to examine the possibility of their dehydration, and to find conditions under which this dried complex is sufficiently soluble in organic solvents to prepare scintillators. As direct exchange of hydrogen for Gd in carboxylic acid molecules is virtually excluded, synthesis of gadolinium carboxylates involved preliminary neutralization of carboxylic acids with a stoichiometric amount of ammonia:

$$HR(o) + NH_4OH(o) = NH_4R(aq) + H_2O,$$
(1)

where HR is a carboxylic acid. The reaction was completed at pH 9.0, when the carboxylic acid fully transformed into the ammonium salt NH<sub>4</sub>R readily soluble in water. Into the precooled aqueous solution of NH<sub>4</sub>R, we added with vigorous stirring the calculated amount of an aqueous GdCl<sub>3</sub> solution. The GdR<sub>3</sub>·nH<sub>2</sub>O precipitate formed by the reaction

$$NH_4R(aq) + GdCl_3(aq) = GdR_3 \cdot nH_2O \downarrow + 3NH_4Cl(aq) (2)$$

was washed with water to remove unchanged substances (HR and GdCl<sub>3</sub>) and the reaction product (NH<sub>4</sub>Cl) until the reaction for Cl<sup>-</sup> anions became negative and then with anhydrous alcohol and acetone to remove the major fraction of water. Then the product was dried in air at room temperature. The water content of the precipitate obtained (Fischer titration) was on the level of 0.4%. The solubility of the synthesized carboxylates in TMB (Table 1) and other organic solvents, however, appeared to be insufficient for preparing scintillators. Analysis of the TGA diagram of all the synthesized gadolinium carboxylates showed that they are resistant to heating to ~250°C. Further heating leads to their decomposition which is complete at 500- $600^{\circ}$ C. The final decomposition product is Gd<sub>2</sub>O<sub>3</sub>. Heating of Gd(2MVA)<sub>3</sub>·nH<sub>2</sub>O to 80°C leads to the removal of water that is not bound in the extractable complex (0.2%), which is followed by weight losses of 0.134% in the temperature range 80-130°C and 0.07% in the range 130–150°C. Further heating of Gd(2MVA)<sub>3</sub> samples did not lead to weight loss up to 250°C. The total weight loss due to water removal was 0.41%. The results obtained confirmed the possibility of removing the major fraction of water from gadolinium carboxylates by thermal dehydration without their decomposition. In Gd(2MVA)<sub>3</sub> samples kept at 140°C for 2 h, the water content was less than 0.01% (Fig. 1, curve 2; Fischer titration). In the above-described experiments, the moisture content of the initial  $Gd(2MVA)_3 \cdot nH_2O$ 

Number of C atoms in acid molecule	Compound	М	% Gd	Solubility in TMB, g l <sup>-1</sup>	pH of synthesis	$T_{\rm m-}, ^{\circ}{\rm C}$	<i>T</i> <sub>dec</sub> -, °C
4	Gd(iBA) <sub>3</sub>	418	37.5	1.33	—		_
5	Gd(2MBA) <sub>3</sub>	460	34.1	0.22	5.1		_
5	Gd(TMA) <sub>3</sub>	460	34.1	0.07	4.62	Does not melt up to 300°C	_
6	Gd(2MVA) <sub>3</sub>	502	31.3	0.35	6.17		250-380
6	Gd(EtBuA) <sub>3</sub>	502	31.3	0.18	5.1		_
6	Gd(HexA) <sub>3</sub>	502	31.3	0.21	5.13	101–103	_
7	Gd(HepA) <sub>3</sub>	544	28.8	0.19	5.57	100–101	_
8	$Gd(2EtHexA)_3$	586	27.8	0.30	5.36	Does not melt up to 300°C	300-500

Table 1. Properties of gadolinium carboxylates

**Table 2.** Solubility of gadolinium carboxylates in  $H_2O$  ([Gd], g l<sup>-1</sup>) and pH of solutions after stirring for 2 h at various temperatures

Compound	Number of C atoms in	25°C		40°C		60°C		80°C	
Compound	acid molecule	pН	[Gd]	pН	[Gd]	pН	[Gd]	pН	[Gd]
Gd(iBA) <sub>3.1</sub>	4	6.3	38.8	6.01	30.2	5.76	20.6	5.12	15.3
Gd(2MBA) <sub>2.96</sub>	5	6.46	8.54	6.16	5.89	5.86	4.29	5.69	2.44
$Gd(TMA)_3$	5	6.45	2.2	5.89	1.72	5.44	1.13	5.21	0.76
Gd(2MVA) <sub>3.08</sub>	6	6.25	1.58	5.8	1.05	5.6	0.65	5.48	0.45
Gd(EtBuA) <sub>3.4</sub>	6	6.26	1.45	6.06	0.907	5.87	0.56	5.68	0.37
Gd(HexA) <sub>3</sub>	6	6.21	0.19	6.19	0.16	5.85	0.14	5.68	0.145
Gd(HepA) <sub>3</sub>	7	5.45	0.05	5.39	0.045	5.43	0.042	5.42	0.046
Gd(2EtHexA) <sub>3.09</sub>	8	4.28	0.19	4.3	0.145	4.30	0.108	4.28	0.99

after washing with alcohol and acetone and before thermal dehydration was 0.41%. However, highly inflammable ethanol and acetone are hardly suitable as solvents for dehydration of gadolinium carboxylate in its production in amount of several tons. Therefore, it was necessary to examine the possibility of removing water directly from the precipitate after its washing with water (moisture content ~60%). We noted that the solubility in water of freshly prepared Gd carboxylates sharply decreases with increasing temperature with simultaneous decrease in pH of the aqueous phase (Table 2). This may be due to hydrolysis of gadolinium carboxylates at elevated temperatures in accordance with the reaction

$$GdR_3 + H_2O \rightleftharpoons Gd(OH)_xR_{3-x}\downarrow + H^+.$$
 (3)

Cooling to room temperature of carboxylate precipitates equilibrated with the aqueous phase did not lead to an increase in their solubility in the equilibrium aqueous phase. Furthermore, with increasing time of solution heating, the solubility of the carboxylate and pH of the equilibrium aqueous phase decreased (Table 3).



**Fig. 1.** Weight loss (% of initial sample weight) of  $Gd(2MVA)_3$  on heating in a nitrogen atmosphere (TG diagrams): (1) sample preliminarily dried in air for 5 days at room temperature ( $22 \pm 1^{\circ}C$ ); (2) sample 1 additionally heated for 2 h at 140°C.

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Heating time (50°C), h	pН	$[Gd], g l^{-1}$
1.5	6.05	1.21
2.5	6.02	1.21
4.5	5.96	1.15
7.0	5.92	1.12
24.0	5.93	1.12
31.0	5.90	1.09
48.0	_	0.8

Table 3. Effect of heating time on the solubility of  $Gd(TMA)_3$  in water and pH of the equilibrium aqueous phase

Comparison of the IR spectra of two samples of gadolinium 2-methylvalerates prepared in accordance with reactions (2) and (3) also confirmed the presence of the OH<sup>-</sup> group in gadolinium 2-methylvalerate that precipitated on heating its aqueous solution. Samples dried in air and calcined for 2 h at 140°C were prepared as mulls in mineral oil and as KBr pellets. The bands in the spectra of the compounds isolated in this study were assigned by comparing the spectra with those of the starting compounds [H2MVA, Gd(OH)<sub>3</sub>] and by analyzing published data [9]. Liquid carboxylic acids are characterized by a broad absorption band with several submaxima in the range  $3000-2500 \text{ cm}^{-1}$ (Fig. 2). Absorption in the range  $2700-2500 \text{ cm}^{-1}$  in the spectrum of H2MVA convincingly confirms the presence of strong hydrogen bridges between the carbonyl and hydroxy groups in carboxylic acid dimers.



**Fig. 2.** IR spectra: (1) Gd(2MVA)<sub>3</sub> prepared by reaction (2) and heated for 2 h at 140°C, (2) H2MVA, (3) Gd(OH)<sub>x</sub>· (2MVA)<sub>3-x</sub> prepared by reaction (3) and heated for 2 h at 140°C, and (4) Gd(OH)<sub>3</sub>.

In the spectra of complexes formed by H2MVA with Gd, the most characteristic bands in this range disappear, and only weak bands indicative of the presence of weak hydrogen bonds remain.

The stretching vibration band of the carbonyl group in H2MVA, manifested at 1710 cm<sup>-1</sup>, disappears upon complexation, with two new bands at 1538 and 1420 cm<sup>-1</sup> appearing instead. These bands correspond to antisymmetric and symmetric vibrations of the COO<sup>-</sup> group in which both O atoms become equivalent. The first of these bands is very characteristic, whereas in the range 1450–1300 cm<sup>-1</sup> there are also bands belonging to other vibrations of the ligand skeleton and to vibrations of mineral oil. To eliminate the absorption bands of mineral oil, we recorded the spectrum of Gd(2MVA)<sub>3</sub> using the KBr technique.

In the IR spectrum of a sample isolated after heating gadolinium carboxylate in water [reaction (3)], there is a strong broad band at about 3390 cm<sup>-1</sup>, corresponding to the stretching vibration of the OH<sup>-</sup> group. A low-frequency shift of this band relative to the OH<sup>-</sup> stretching vibrations in gadolinium hydroxide (Fig. 2) indicates that the compound isolated by heating the aqueous solution is the hydrolysis product of the salt Gd(2MVA)<sub>3</sub> and has the composition Gd(OH)<sub>x</sub>(2MVA)<sub>3-x</sub>, where x = 0.1-0.2 (chemical analysis data).

The spectra of Gd(2MVA)<sub>3</sub> and Gd(OH)<sub>x</sub>(2MVA)<sub>3-x</sub> (Fig. 2) differ not only in the range 3500–3000 cm<sup>-1</sup>, but also in the range 1000–800 cm<sup>-1</sup>. This is most probably due to the fact that out-of-plane vibrations of the O–H···O group are observed just in this range. The presence of medium-intensity bands in the range 3500–3000 cm<sup>-1</sup> in the spectrum of the complex isolated after heating the aqueous solution (Fig. 2) confirms the presence of strong hydrogen bonds and hence the composition of the hydrolysis product.

Similar hydrolysis of gadolinium carboxylates will apparently occur in the course of thermal drying of wet precipitates (Gd concentration in the equilibrium aqueous phase was 1.56 g l<sup>-1</sup>). The presence of such partially hydrolyzed carboxylate species is undesirable because of their tendency to polymerize and form difficultly soluble precipitates. This may lead to the loss of the scintillator transparence with time. Therefore, to minimize the Gd hydrolysis in the course of thermal drying, it was necessary to preliminarily remove the major amount of water from Gd(2MVA)<sub>3</sub> under "mild" conditions when hydrolysis is less pronounced. Drying

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Solvent	Scintillation additive, $g l^{-1}$	Scintillator density, g ml <sup>-1</sup>	Light output relative to anthracene, %	Transparence $L^{430 \text{ nm}}$ , m
TMB	BPO (4)	0.88	80.0	12.0
Dodecane	BPO (4)	0.75	33.0	30.0
Mineral oil	BPO (4)	0.838	33.0	10.0
1-Methylnaphthalene	_	1.01	_	0.2
TMB(10%) + dodecane (90%)	_	0.764	_	20.0
TMB(15%) + dodecane (85%)	_	0.771	_	24.0
TMB(20%) + dodecane (80%)	BPO (4)	0.78	61.0	24
TMB(35%) + dodecane (65%)	_	0.8	65.0	27.0
TMB(20%) + mineral oil (80%)	BPO (5)	0.846	52.0	10.0
TMB(30%) + mineral oil (70%)	BPO (5)	0.851	63.0	10.0
PXE (20%) + dodecane (80%)	_	0.798	_	9.0

Table 4. Light output relative to anthracene and transparence of solvents intended for preparing scintillators

in an air flow at room temperature in a thin bed  $(\sim 5 \text{ mm})$  for 3–4 days allowed the moisture content to be decreased from 61 to 0.4-0.5%. After that, the dried precipitate was placed in an oven and heated for 2 h at 140°C. The moisture content of the final product did not exceed 0.01%. The solubility of Gd(2MVA)<sub>3</sub> prepared by this procedure was as follows  $(g l^{-1})$ : in TMB, 0.36; in PXE, 0.02; in dodecane, 0.17; in octane, 0.98; in hexane, 0.175; in water, 1.58; in acetone, 0.078; in anhydrous ethanol, 0.94; in 20% TMB + 80% dodecane mixture, 0.33; and in 20% PXE + 80% dodecane mixture, 0.22. It should be noted that the solubility of Gd(2MVA)<sub>3</sub> in organic solvents appreciably varies with time. For freshly prepared samples, it is higher than for samples dried at elevated temperatures and stored for a certain time.

In any case, to prepare a scintillator it was necessary to increase the solubility of Gd(2MVA)<sub>3</sub> to at least 1 g  $l^{-1}$ . It was noted previously [1] that the readily soluble Gd complex with H2MVA is Gd(2MVA)<sub>3</sub>. 3H2MVA. Therefore, to anhydrous Gd(2MVA)<sub>3</sub> we added a stoichiometric amount of anhydrous H2MVA (after vacuum distillation) and appropriate organic solvent. By so doing, we prepared an organic phase with the Gd concentration  $[Gd](o) > 50 \text{ g } l^{-1}$ . Further studies showed that additions of neutral organophosphorus compounds (NOPCs) such as phosphates, phosphonates, and phosphine oxides also led to an increase in the solubility of  $Gd(2MVA)_3$  in organic solvents. The stability of the optical constants of the scintillators decreased in the order phosphine oxide > phosphonate > phosphate, in accordance with variation of the extraction constants of rare-earth elements with these extractants.

# Properties of Gd-Loaded LOSs Prepared by Dissolution of Anhydrous Gadolinium 2-Methylvalerate in Organic Solvents

The most frequently used organic solvent for preparing scintillators is TMB [7]. At the same time, TMB has a number of significant drawbacks restricting its use in the limited space of underground laboratories and near nuclear reactors: low flash point (49°C), toxicity, poor compatibility with organic glass used as structural material of the detector, and low H : C ratio. The flash point of pure PXE is high (149°C), but it has low H : C ratio and high viscosity and density; furthermore, it poorly dissolves gadolinium carboxylates.

The properties of the above solvents can be improved by mixing them with paraffin hydrocarbons (dodecane, mineral oil). Some properties of solvents that we used for preparing Gd-loaded LOSs are given in Table 4. The final choice of PPO as scintillation additive is governed by its availability and relatively low cost.

It was important to know whether gadolinium 2-methylvalerate introduced into an organic solvent would affect the energy transfer from the solvent to the scintillation additive. For this purpose, we recorded the absorption spectra of Gd(2MVA)<sub>3</sub> (1.2 g  $l^{-1}$ ) and PPO (0.01 g  $l^{-1}$ ) in cyclohexane in a 1-cm-thick cell (Fig. 3). Comparison of these spectra at 300 nm gave

Solvent	Gd concentration, g $l^{-1}$	Stabilizing additive	Storage time, days	$L^{420 \text{ nm}}, \text{ m}$
	2.0		0	8.0
TMB	2.0		40	10.0
	2.0	_	285	14.0
	2.0		Stabilizing additive    Storage time, days      0    0      40    285      450    0      IR <sub>3</sub> ·1HR    40      220    0      IR <sub>3</sub> ·2HR    0      IR <sub>3</sub> ·2HR    0      IR <sub>3</sub> ·2HR    0      IR <sub>3</sub> ·2HR    0      IR <sub>3</sub> ·3HR    0      IR <sub>3</sub> ·3HR    0      IR <sub>3</sub> ·2HR    0      IR <sub>3</sub> ·2TIAPO    0      IR <sub>3</sub> ·3TIAPO    0      210    0	8.0
	1.4		0	12.0
	1.4	GdR <sub>3</sub> ·1HR	40	20.0
	1.4		220	17.0
	1.4		0	15.0
	1.4	CdD 211D	40	20.0
TMB (35%) + dodecane(65%)	1.4	OdK <sub>3</sub> ·2HK	285	20.0
	1.4		450	10.0
	2.1		0	17.0
	2.1		40	18.0
	2.1	Gak <sup>3</sup> .2HK	285	20.0
	2.1	Oncentration, g 1  Stabilizing additive    2.0	450	14.0
	1.5		0	15.0
TMB (20%) + dodecane(80)% +	1.5	CdD 211D	125	16.0
PPO (1.5 g l <sup>-1</sup> )	1.5	Ouk <sub>3</sub> ·2HK	480	18.0
	1.5		661	14.0
PXE (20%) + dodecane(80)%	1.6		0	16.0
	1.6	Gak <sub>3</sub> ·IIIAPO	210	11.0
	1.6		0	14.0
	1.6	Gak <sub>3</sub> ·211APO	210	11.0
	1.6		0	10.0
	1.6	Ouk <sub>3</sub> ·311AFO	210	8.0

**Table 5.** Influence of the storage time of Gd-loaded LOS samples on their transparence. HR is 2-methylvaleric acid, and TIAPO is triisoamylphosphine oxide

the following results: light absorption by PPO about  $1.2 \times 10^2$  and that by Gd(2MVA)<sub>3</sub> about 0.15.

Evidently, the light absorption caused by the presence of  $Gd(2MVA)_3$  is negligibly low compared to the light absorption by the scintillation additive. Hence, introduction of Gd into LOS does not affect the energy



**Fig. 3.** Absorption spectra of (1-3) Gd(2MVA)<sub>3</sub> and (4) PPO in cyclohexane. Concentration, g l<sup>-1</sup>: [Gd](o): (1) 1.2, (2) 1.85, and (3) 2.7; PPO: (4) 0.01.

redistribution between the solvent and the scintillation additive. Therefore, the spectra of the pure and Gdloaded solvents differ insignificantly.

The stability of Gd-loaded LOSs was studied by intermittent sampling during a long period and measuring the transparence and light output of the samples. The scintillator degradation can be judged from variation of these parameters with time. Data in Table 5 show that the high transparence of the scintillators is preserved after prolonged storage at room temperature. The use of a scintillating additive (PPO) does not affect the scintillator stability (Table 5). At the same time, at elevated temperatures (50°C), noticeable degradation of the scintillator is observed in the shortwave region of the spectrum (Fig. 4a). It increases in the case of contact of the scintillator with possible structural materials of the detector, stainless steel and organic glass (Fig. 4b), with a mixture of TMB with dodecane used as solvent. As the mixture of PXE with dodecane is better compatible with organic glass, this



Fig. 4. Absorption spectra of solutions of  $Gd(2MVA)_3$ : 3TIAPO in 35% TMB + 65% dodecane mixture, [Gd](o) = 3.6 g l<sup>-1</sup>: (1) after preparation and (2) after keeping for 30 days at 50°C. Storage: (a) in glass vessels without contact with structural materials of the detector and (b) in the presence of organic glass and stainless steel.



**Fig. 5.** Transmission spectra of solutions of  $Gd(2MVA)_3$ : 3TIAPO in 20% PXE + 80% dodecane mixture. Time of storage at 20°C (nitrogen atmosphere, protection from daylight) 0, 33, 60, 130, 174, 214, 242, 350, and 398 days (the spectra coincide).

mixture was our final choice. The use of NOPCs as additives allows preparation of stable scintillators with this mixture. Long-term tests in Gran Sasso National Laboratory (Italy) and Saclay (France) showed that storage of scintillator samples based on  $Gd(2MVA)_3$ . *n*TIAPO ) (n = 1, 2, 3) at 30°C (Fig. 5) did not lead to



**Fig. 6.** Transmission spectra of solutions of  $Gd(2MVA)_3$ . 3TIAPO in 20% PXE + 80% dodecane mixture in relation to the time of storage at 40°C (nitrogen atmosphere, protection from daylight). Storage time, days: (1) 0, (2) 33, (3) 60, (4) 130, (5) 174, (6) 214, (7) 242, (8) 350, and (9) 398.

any changes in their absorption spectra. At the same time, the optical properties of the samples stored at 40°C under identical conditions (in sealed vessels under nitrogen, with protection from light) became worse (Fig. 6). Taking into account the fact that the temperature in underground rooms where the detectors are intended to be arranged will be maintained on the level of +20°C, the scintillators obtained can be recommended for detection of reactor antineutrino. After successful completion of tests of Gd-loaded LOSs with small volumes ( $\sim 1$  l), we prepared an enlarged batch of the scintillator (32 l) with a gadolinium concentration of 0.85 g  $l^{-1}$  ( $\approx$ 0.1%) and delivered it to Saclay (France) for testing the compatibility of the scintillator with the structural material of the detector (organic glass). The scintillator was placed in a vessel of Acryl GS-233 organic glass (Rhome), purged with nitrogen, hermetically sealed, and shielded with a dark material to protect from daylight. Samples will be withdrawn through a special hole at 6-month intervals during a long period to measure the scintillator transparence. The first four measurements have not revealed any signs of the scintillator instability.

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