# X-ray detection capability of bismuth-loaded plastic scintillators

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## Abstract

We evaluated the high-energy X-ray detection capabilities of Bi-loaded plastic scintillators. The detection efficiency for 67.4 keV X-rays was successfully increased by increasing the Bi concentration. The detection efficiency of a plastic scintillator loaded with 10 wt % Bi was comparable to that of a commercially available plastic scintillator loaded with 5 wt % Pb, NE-142. A subnanosecond time resolution was achieved, and no long scintillation component appeared with Bi loading. These results indicate that Bi loading is an effective method of enhancing the detection efficiency for high-energy X-rays while preserving the timing properties of plastic scintillators.

## 1. Introduction

The demand for fast detection of X-ray synchrotron radiation has increased due to the widespread use of intense beams and time-resolved measurements. Detection signals with fast decays and no long tails (afterglow) are desired for such applications. For low-energy X-rays, that is, those with energies less than 20 keV, an avalanche photodiode (APD) with a thin active layer is an appropriate detector.[1,2)] For X-rays with higher energies, however, sufficient detection efficiency cannot be achieved using APDs.[3)] Scintillation detectors equipped with scintillators with fast scintillation decays and no long components could present an elegant solution to such a technological challenge.

For this purpose, some of the authors (the Japanese group) have evaluated novel scintillation materials, including inorganic crystals exhibiting fast self-trapped exciton emission[4)] or Auger-free luminescence,[5,6)] organic–inorganic hybrid compounds with quantum-well structures,[7)] and plastic scintillators loaded with inorganic nanoparticles.[8,9)]

To complete the spectrum of available solutions, this paper focuses on plastic scintillators loaded with homogenously dispersed organometallic compounds, as plastic scintillators with enhanced detection efficiencies are promising candidates for such usage. Furthermore, this technology is very cost-efficient as the chemical cost is low and a very large variety of shapes and volumes is readily accessible. In order to enhance the detection efficiency for high-energy photons, incorporating heavy metal elements as organometallic compounds into plastic

scintillators is an efficient method.[10] This approach solves the issues of low density and low effective atomic number of plastic scintillators, which represent the major limitations of gamma spectrometry. Recently, some of the authors (the French group) succeeded in manufacturing Bi-loaded plastic scintillators to enhance the gamma-ray sensitivity.[11] These materials were the second generation of heavy-metal-loaded plastic scintillators embedded in an X-ray imaging system for the Laser Mégajoule.[12,13] In this study, we evaluated the applicability of Bi-loaded plastic scintillators for synchrotron X-ray detection. We focused on two points: the dependence of detection efficiency on the Bi concentration and the presence (or absence) of long tails in the time-resolution curves. The detection capabilities of the Bi-loaded scintillators were compared with that of a commercially available plastic scintillator for high-energy photons, NE-142, which is loaded with 5 wt % Pb and is equivalent to BC-452 or EJ-256 plastic scintillators.

## 2. Experimental methods

The raw materials were purchased from Sigma-Aldrich, except for the triphenyl bismuth ($BiPh_3$), which was acquired from PHDS Co. The styrene monomer was distilled over $CaH_2$ under reduced pressure to eliminate inhibitors and impurities. The other reagents were used without further purifications. Bi-loaded plastic scintillators with different Bi concentrations (2 wt % Bi, 5 wt % Bi, or 10 wt % Bi) were fabricated by using the following procedure: Fluorescent dyes [2,5-diphenyloxazole (PPO) and 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP)], triphenyl bismuth ($BiPh_3$), and styrene monomer were mixed and inserted in a suitable round-bottom flask. The mixed solution was placed under a nitrogen atmosphere and subsequently frozen using liquid nitrogen, and multiple freeze–pump–thaw cycles were performed to achieve total degassing. The degassed solution was poured into a cylindrical glass mold containing a small quantity of initiator for polymerization. The filled mold was purged with nitrogen, sealed, and placed into an oven at 40 or 45 °C for 15–30 days. After total polymerization, the mold was cooled down to room temperature and then shattered to free the plastic piece. The cylindrical samples with a diameter of 18 mm and thickness of 9 mm were shaped and polished. The details of the fabrication method were described in a previous paper.[11]

Pulse height spectra featuring a $^{137}Cs$ source (662 keV, 200 kBq) were acquired using a photomultiplier tube (PMT; Hamamatsu H1949-51) operating at negative voltage and powered by an Ortec 556 high voltage supply. The plastic scintillator was optically coupled to the PMT with optical grease, and the radioactive source was located 10 cm away from the sample. Output signals were recorded unfiltered using a custom made acquisition setup, operating at 800 MHz and 10 bit. The acquisition process was performed during 5 min.

Scintillation spectra under X-ray irradiation were observed by using an X-ray generator operated at 80 kV and 2.5 mA and a Peltier-cooled-CCD (Andor DU-420-BU2) coupled with a grating monochromator (Oriel Instruments SR163, 285 grooves/mm, blaze wavelength of 280 nm). The temporal scintillation profiles were obtained through a single-photon counting method by using a pulsed X-ray beam as an excitation source.[14]

The high-energy X-ray detection capability was evaluated using a synchrotron radiation X-ray beam at Beamline AR-NE7A of the Photon Factory, KEK, Japan. The X-ray energy was set at 67.4 keV. The single-bunch-mode operation was used, and the X-ray pulse period was 1258 ns. The beam spot size was approximately 1 mm in diameter. The fluence of X-ray photons was monitored with a photodiode in the upstream part of the beamline. The scintillators were

attached to a PMT (Hamamatsu R7600) with an optical grease. For the pulse-height spectrum measurements, the detection signals were amplified with a charge-sensitive amplifier (Canberra 2005) and a main amplifier (Ortec 572A). The amplified signals were fed to a multichannel analyzer (MCA; Amptek MCA-8000D) in order to obtain the pulse-height spectra. The detection efficiency was estimated by comparing the counting rate of the scintillation detectors equipped with sample scintillators and that of the detector equipped with a 5-mm-thick NaI:Tl scintillator, for which the detection efficiency is unity. To obtain the time-resolution curve, the detection signal was amplified with a fast preamplifier (Ortec VT120A). The timing signal indicating the X-ray pulse arrival was supplied by the accelerator. The signal timings were determined with a constant fraction discriminator (CFD; Ortec 935). The time difference between the arrival and detection signals was converted into a voltage with a time-to-amplitude converter (Ortec 566). Finally, the converted signal was fed to the MCA in order to obtain the time-resolution curve. The detection capability of the sample scintillators was compared with that of a 1-mm-thick commercial plastic scintillator, NE-142 (loaded with Pb at 5 wt %, OKEN).

## 3. Results and discussion

Figure 1 shows the scintillation spectra. Characteristic bands at approximately 420 and 440 nm due to the emission of POPOP are observed for all of the samples. No emission is observed from the PPO, which typically occurs at 365 nm, indicating that an effective Förster energy transfer is performed from PPO to POPOP.

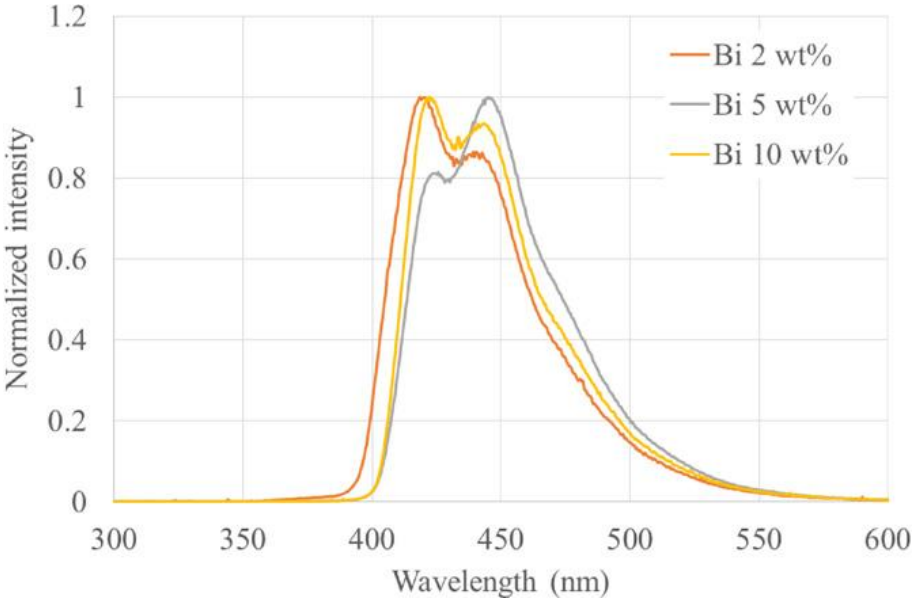


**Fig. 1.** Scintillation spectra.

The production of high-energy X-ray detectors with excellent timing properties is limited by the time responses of the scintillators. One component that is essential in order to achieve excellent timing properties is a detector with a very short response time. This short response time is why plastic scintillators are attractive to begin with, as their decay time constants can be tuned to nanoseconds or even lower and they are amongst the fastest scintillation materials. Figure 2 shows the temporal scintillation profiles. The decay was fitted with a sum of two exponential decay functions. The decay time constants and relative intensities were 2.2 ns (62%) and 11 ns (38%), 2.1 ns (69%) and 13 ns (31%), and 1.9 ns (65%) and 7.9 ns (35%) for

the plastic scintillators loaded with 2 wt % Bi, 5 wt % Bi, and 10 wt % Bi, respectively. The temporal profiles were essentially the same for all of the samples, which indicates that incorporating $BiPh_3$ did not produce undesirable long components. This observation does not conflict with the classic theory that heavy-atom loading tends to decrease the fluorescence decay time constant. Indeed, the excited states in the polystyrene host that have long decay time constants are more likely to transfer their energies to the organometallic compound and to be quenched by Bi even at low Bi concentration, leading to the absence of the long component for all the samples. The time profiles were almost the same for the scintillators with different Bi concentrations. This result is explained in the following: the quenching by $BiPh_3$ occurs in competition with the energy transfer from the polystyrene host to the primary phosphor, DPO. The quenching does not compete with the energy transfer from the DPO to POPOP or the luminescence at POPOP, because the quenching in competition with these processes would lead to different time profiles for different Bi concentration.

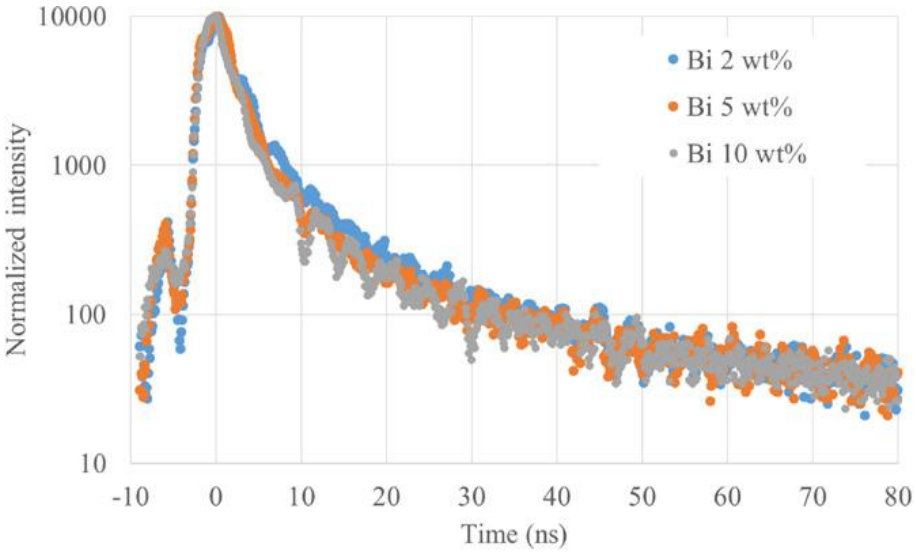


**Fig. 2.** Temporal scintillation profiles.

Following these promising results, we evaluated the time-resolution curves of our scintillators under standard conditions in a synchrotron facility. Exposure to a high-energy X-ray beam (67.4 keV) was recorded with the time-resolved acquisition set-up. The time-resolution curves of the scintillation detectors equipped with the Bi-loaded plastic scintillators are shown in Fig. 3. The main result is that a subnanosecond time resolution was successfully achieved for all the scintillators. Expectedly, no long tails in the time-resolution curves were observed even at high Bi concentrations, which is consistent with the conclusion based on Fig. 2 that the incorporation of $BiPh_3$ does not yield an undesirable long scintillation component.

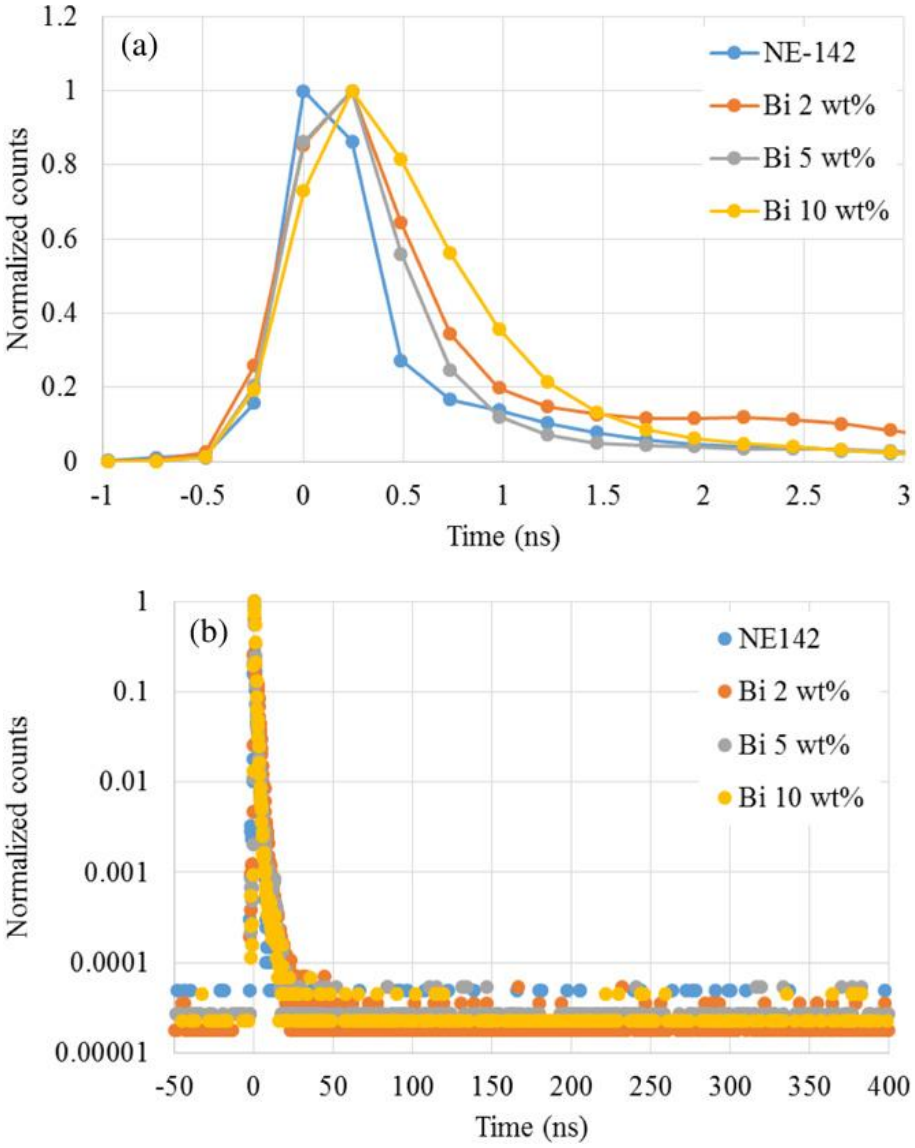


**Fig. 3.** Time-resolution curves of scintillation detectors equipped with sample scintillators for 67.4 keV X-ray excitation on (a) short and (b) long time scales.

Figure 4 shows the pulse-height spectra of the scintillators exposed to a 67.4 keV X-ray beam. The photoelectric peak position shifts to lower channels as the Bi content increases, which indicates that the light yield is lower at higher Bi concentrations. The photoelectric peak are observed at channels 180, 140, and 80 for the plastic scintillators with 2 wt % Bi, 5 wt % Bi, and 10 wt % Bi, respectively, whereas that for NE-142 is observed at channel 350. This discrepancy could be explained by the use of NE-142, which is nine times thinner than the Bi-loaded plastics, limiting the self-absorption of the scintillation photons. Because the scintillation wavelengths of NE-142 and of the sample scintillators are similar, the light yield could be estimated by comparing the channel numbers of the photoelectric peaks in the pulse-height spectra. Using the reported light yield of 32% of the yield of anthracene for NE-142,[15] the light yields of the Bi-loaded plastic scintillators were estimated to be 16, 13, and 7% of the yield of anthracene for 2 wt % Bi, 5 wt % Bi, and 10 wt % Bi concentrations, respectively. In previous literature, a similarly synthesized Bi-loaded plastic scintillator (1.8 wt % Bi) was reported to exhibit 99% of the yield of EJ-256 (equivalent to NE-142).[11] Figure 5 shows the pulse-height spectra of the scintillation detectors equipped with the Bi-loaded plastic

scintillators for 662 keV gamma rays from $^{137}$Cs. The Compton edge of the Bi-loaded plastic scintillators was much closer to that of EJ-256, and this result is consistent with that reported in the previous paper.[11] The estimated light yield of the Bi-loaded plastic scintillators for 67.4 keV X-rays is lower than those estimated at the Compton edge for 662 keV gamma rays from $^{137}$Cs, as shown in Fig. 5. This difference may originate from two sources: one is the non-proportionality of the scintillation light yield, which is currently under investigation.[16] The other is the difference between the thicknesses of the scintillators: the NE-142 sample was nine times thinner than the Bi-loaded plastics, which limited the self-absorption of the scintillation light in the case of NE-142. Figure 6 shows the absorption spectra of the Bi-doped scintillators. According to Fig. 1, the most of the scintillation was observed between 400 and 450 nm. We observed a steep rise in the absorbance at approximately 420 nm. Hence, most of the scintillation photons at short wavelength region are absorbed inside the scintillators. The full width at half maximum (FWHM) energy resolutions of 67.4 keV X-ray were 39, 49, 57, and 71% for NE-142 and for the plastic scintillators loaded with Bi at 2, 5, and 10 wt %, respectively. The FWHM energy resolution was slightly worse with higher Bi loading, possibly due to the decrease in the light yield.

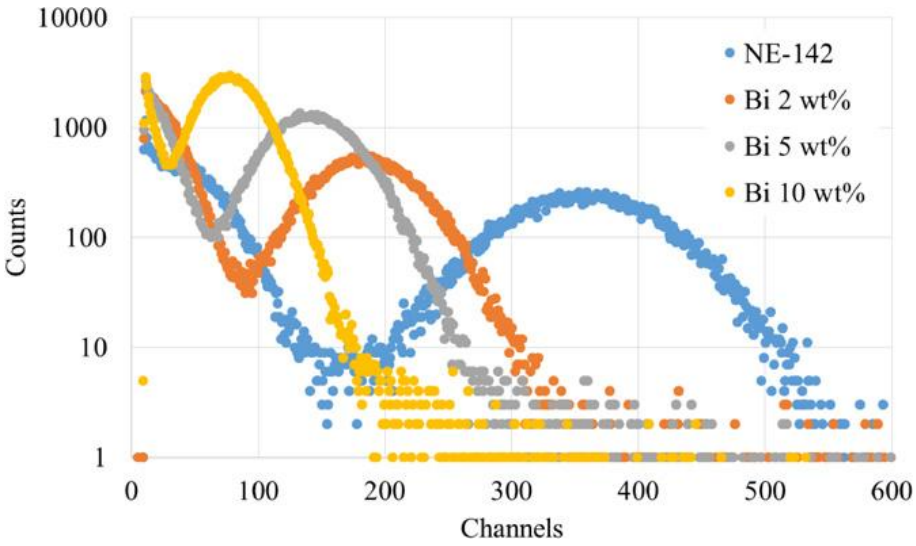


**Fig. 4.** Pulse-height spectra of scintillation detectors equipped with sample scintillator or NE-142 for 67.4 keV X-ray.

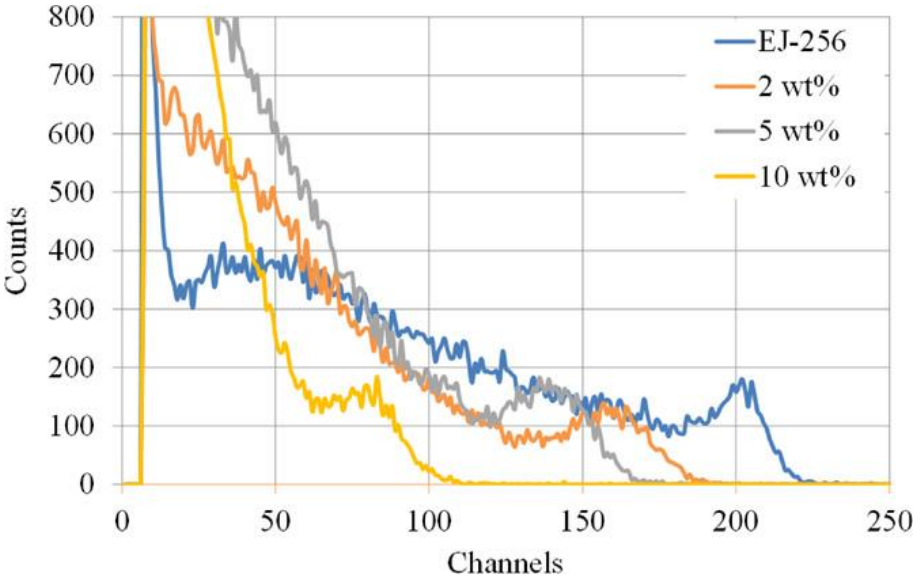


**Fig. 5.** Pulse-height spectra of Bi-loaded plastic scintillators and EJ-256 with $^{137}$Cs gamma source.

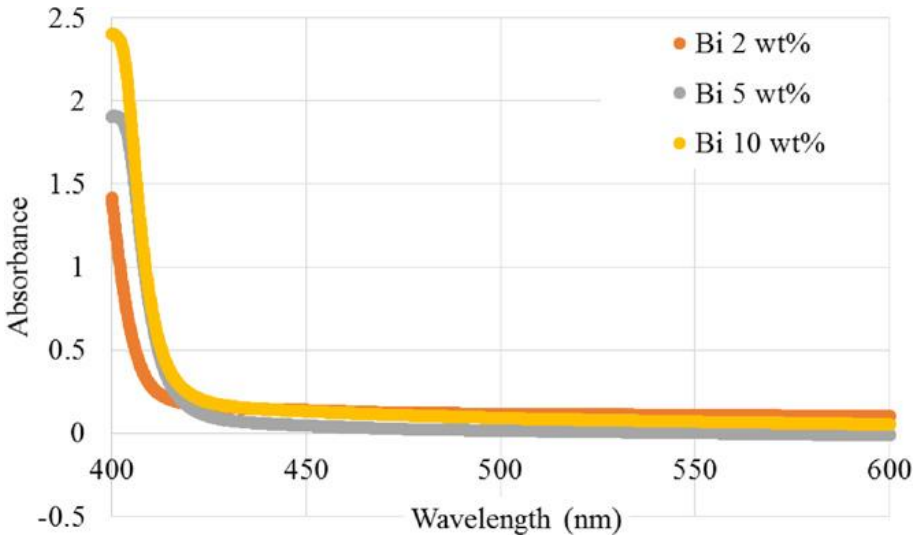


**Fig. 6.** Absorption spectra.

The counting rate evolution in this investigation is in perfect concordance with those reported in previous literature. As shown in Fig. 4, the total counts are higher for the plastic scintillators with higher Bi loading. Table I summarizes the detection efficiencies estimated based on the counting rates of the scintillation detectors equipped with sample scintillators and on that of the detector equipped with the 5-mm-thick NaI:Tl scintillator, for which the detection efficiency can be assumed to be unity. The scintillator thicknesses are also shown. The detection efficiency was successfully enhanced by increasing the Bi content. Taking into account the thickness difference, the detection efficiency of the plastic scintillator with 10 wt % Bi is comparable to that of NE-142. This achievement will enable the acquisition of reliable data sets with less statistic collection, which will decrease the time consumption of the desired X-ray beam experiment. Combined with the results of the time-resolved experiments, these results indicate that the loading of plastic scintillators effectively enhances

the detection efficiency for high-energy X-ray photons without degrading the timing properties.

| | Detection efficiency (%) | Thickness (mm) |
|---|---|---|
| NE-142 | 3.9 | 1 |
| Bi 2 wt % | 18.5 | 9 |
| Bi 5 wt % | 26.7 | 9 |
| Bi 10 wt % | 34.0 | 9 |

**Table I.** Detection efficiencies of scintillation detectors equipped with Bi-loaded scintillators or NE-142 for 67.4 keV X-ray.

## 4. Conclusions

The high-energy X-ray detection capabilities of Bi-loaded plastic scintillators were evaluated. The light yield gradually decreased with increasing Bi concentration. The detection efficiency was successfully enhanced by the Bi loading, and that of the plastic scintillator with 10 wt % Bi for 67.4 keV X-ray photons was comparable to that of NE-142. In addition, no long scintillation component was observed for the temporal profiles of the scintillation and time-resolution curves. These results indicate that Bi-loaded plastic scintillators are applicable for high-energy X-ray detection in which good time resolution is necessary and long tails in the detection signals should be negligible.

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