ASSAY OF LUMINESCENT BORAZINE AND BORAZARENE DERIVATIVES AS SLOW NEUTRON SCINTILLATORS *

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Summary

N-trimethyl B-tri(diphenyl), N-triphenyl B-tri(diphenyl), N-triphenyl B-tri(alpha-naphtyl) borazines, and hydroxiborazaro phenanthrene and bis 2-1 borazaro-2-naphtyl ether, were assayed in benzene solution and as solid films for scintillation counting of thermal neutrons moderated with paraffin from the reaction $Li^7(d,n)Be^8$. A background of gamma radiation was present, partly from the reaction $Li^7(p,gamma)Be^8$. Absolute gamma and neutron flux measurements of the source were made, using gamma ray spectrometry and foil activation. Characteristic counting curves and absolute counting efficiencies were obtained for several liquid and solid scintillators. Also, studies of the concentration effects, geometrical and dimensional factors, etc. were made using a Po-Be and a Ra-Be source and several gamma ray sources. Finally, actual tests based on the aforementioned experiments were made in a nuclear critical facility and excellent results were obtained.

Introduction

In previous works[1], we proposed the use of several borazine and borazarene derivatives with fluorescent properties as slow neutron detectors considering their advantages as scintillators with boron atoms in their molecules. Specially purified borazines, containing fluorescent groups (B-tri-(diphenyl) -N-trimethyl-borazine, B-tri (diphenyl)-N-triphenylborazine, B-tri(α-naphtyl)-N-trimethylborazine)[2], and borazarenes with higher stability and boron content (Bis 2, 1-borazaro 2-naphtyl ether and 9-10 hydroxiborazaro-phenanthrene)[3] were tested with regard to their fluorescence spectra, quantum yield, etc.[4]. Some preliminary assays were also performed to determine their possible applications as scintillators[5].

Subsequently, more elaborate assays with solutions and solid films were carried out in order to perform actual tests of the scintillators with counting equipment. No attempts were made to optimize conditions concerning the construction of the detectors, their attachment to the rest of the counting equipment, or the counting technique itself. Special precautions which are usually adopted with commercial detectors, as well as the use of B^{10} enriched substances, could be applied which would greatly increase the performance of these substances.

We consider the promising results reported here as an introductory step in the study of polymeric fluorescent borazine and borazarenes which is now in progress in our laboratory.

This paper includes:

a) Preparation of detectors (solid or liquid) of adequate thickness or concentration and shape.

b) Determination of counting spectra with the solid films or liquid cells in a conventional scintillation counting apparatus with irradiation by thermal neutrons from different sources.

c) Determination of the gamma ray sensitivity of these substances, as well as the verification of the gamma radiation which accompanies the neutrons sources, and calculation of relative n/γ efficiencies.

d) Determination of the absolute flux of thermal neutrons onto the scintillators by indium foil activation and calculation of the absolute

* Presented at the 13th Nuclear Science Symposium, Boston, Mass., October 1966.

I.EEE. Transactions on Nuclear Science. Feb. 1967. Vol NS-14, N° 1.

counting efficiencies for thermal ne rons.

Experimental

1) Chemicals:

Borazines and borazarenes were epared and purified as already reported. Benze p.a. was specially purified as is usual for s intillation use.

2) Preparation of Solid Films:

Solid films were obtained by the fusion of crystals, by the evaporation of solutions, and by the distribution and pressing of layers of small crystals. Unfortunately, all these methods failed to give uniform films with pr per transparency. The most promising results were obtained with glassy transparent films of bor zarenes which were prepared by cooling melte crystals. However, these films had a tendency to crack on standing.

The best results were obtained ing a lucite cell (Fig. 1) where small crystals w e distributed as uniformly as possible. The ce was closed, pressed(5kg/cm^2), and sealed with lu te cement.

3) Liquid Cells:

Sealed Pyrex glass cells were u ed (Fig. 2). These cells had poor light collectio because the optical windows were not perfectly p nar or of uniform thickness, and their walls h d no reflectors.

Other tests were made with diff rent types of cells (Fig. 3) in order to obtain a better optical contact between the scintill tors and the phototube; corresponding correct on factors were introduced for these cells. Th cells were filled in a dry-box and either degas d by the freeze-thaw method in a vacuum line by bubbling through dry nitrogen. The mposition and other data of the counters are i luded in Table I.

4) Counting Apparatus:

The detectors were attached to RCA 6655A photomultiplier tube which was opera d with a cathode follower preamplifier and a abilized power supply. The pulses were studi l either with a Nuclear Data 512 multichannel analyzer which had an IBM typewriter and Moseley plotter readout,or with a single channel analyzer.

5) Neutron Sources:

A Ra-Be (10^5n/sec) or a Po-Be (10^4n/sec) source was used in some experiments. The source was placed in the center of a paraffin cube which was 25 cm on a side. The final moderated flux on the detector from these sources was too low for efficiency studies to be carried out.

In the absolute neutron efficiency experiments, neutrons were obtained from the nuclear reaction $Li^7(d,n)Be^8$ using a Li target and a Cockcroft-Walton machine operated at 1 MV potential and 50 microamperes current. To decrease the gamma radiation which was also present, partly originating from the $Li^7(p,\gamma)Be^8$ reaction on the H^2 impurity in the D^2, 1 inch of lead was placed around the phototube.

Counting experiments were also made in a nuclear critical facility (CNEARAO, enriched uranium bars in a water tank and graphite). The detector was placed about 150 cm from the external graphite wall.

6) Experiments on Composition, Geometry,etc.:

a) Concentration of liquid scintillators: Different concentrations of scintillator in the same cell were tested with a moderated Po-Be source and a Co^{60} source. Plots of counts/minute vs. concentration were obtained from integral counting curves. Fig. 4 shows a typical curve for 9-10 hydroxiborazaro phenanthrene which indicates that about 4 g/l is the most favorable concentration. Tests with the other scintillators gave similar results except for B(α-naphtyl) N-methylborazine which shows a continuous increase in counting rate up to at least 15 g/l.

b) Influence of solution thickness: Experiments were made with 10,25 and 50 mm thick cells with solutions of a constant composition. The results (Fig. 5) obtained with a moderated Po-Be source and a Co^{60} source indicated a favorable cell thickness would be 25 mm in the case of a solution of hydroxiborazaro phenanthrene.

c) Thickness of solid films: Using increasing amounts of material, solid films were

obtained with thicknesses from 5 to 22 mg/cm^2 for B(α-naphtyl) N-methyl-borazine. These films were tested in the manner mentioned above. The results (Fig. 6) indicated a maximum n/γ ratio which corresponded to a thickness of approximately 6 mg/cm^2. However, because of difficulties in the construction of the films, only thicknesses of 7-9 mg/cm^2 were tested for efficiency.

d) Characteristic counting curves:

Counting curves for thermal neutron radiation were obtained with a Nuclear Data multichannel analyzer or with a single channel analyzer and are shown in Fig. 7. The source of the neutrons is indicated on the figures. In order to know the sensitivity for different gamma ray energies, counting curves, were obtained by irradiating the detectors with gamma rays from Cs^{137} and Co^{60} sources and from the $Li^7(p,\gamma)Be^8$ reaction using a Cockcroft-Walton accelerator. The same conditions existed during the neutron irradiations.

Typical counting curves are shown in Fig. 8, and from intersections P,P' and P'' for each scintillator, calibration curves were plotted (Fig. 9). To establish adequate bias points to discriminate against the gamma radiation, these gamma calibration curves were used together with data on the gamma ray energies accompanying each source of neutrons. In the case of the neutrons obtained with the accelerator, gamma ray energies up to 17 Mev were observed (NaI(Tl) detector), but 95% of the counts corresponded to energies lower than 12 Mev.

7) Calculation of Absolute Counting Efficiencies:

In order to obtain the counting efficiency, $\mathcal{E} = \frac{\text{counts} \times 100}{\text{incident neutrons}}$, the actual flux of thermal neutrons on the detectors was measured by indium foil activation. Indium foils of approximately 1 cm^2 in area and 100 mg by weight were placed in the same positions as the detector; the resulting activity was measured in a 4π proportional counter. Counting curves from the accelerator experiments were integrated and the difference between the neutron [$Li^7(d,n)Be^8$] and gamma ray [$Li^7(p,\gamma)Be^8$] counts were used to calculate $\mathcal{E}$. The results are summarized in Table II.

8) n/γ Efficiency Factor:

In the most important application of a thermal neutron detector, which is, undoubtedly, in nuclear reactors, the ratio of discrimination, n/γ, is the preponderant parameter. Results from the integrated counting rates are shown in Table II. It can be seen that the gamma ray counts are only 1-3% of the total counts.

Discussion

Analysis of counting curves and efficiency values indicate a promising behaviour in the tested scintillators. Higher counting rates are observed for the liquid cells; the lower values for the solid films must be attributed to their deficient optical properties, but nevertheless, their low gamma ray response can be considered highly satisfactory with respect to the n/γ efficiency factor.

Since the procedure used for the evaluation of gamma ray background was only approximate, the gamma ray counting rates deduced for the neutron counting were surely larger than the actual values accompanying neutron radiation; thus, efficiencies reported are probably lower than the actual ones. The values of the pulse height discrimination for gamma rays, even though they are a small percentage, could be increased with simple counting equipment, but better values can be obtained with pulse shape discrimination or with equivalent systems.

Many improvements could be made to the work here reported. For example, use of a source of neutrons with a negligible gamma ray background would allow much easier and more precise determinations of detection efficiencies. The cells should be constructed with exactly planar windows and with efficient wall reflectors.

With the solid films, our aim was to obtain transparent, uniform films with enough boron content to have high neutron and low gamma ray absorption characteristics and to have a minimum of light losses. Better results could be achieved with fluorescent, polymeric glassy borazines and

borazarenes, as we are now trying) do in our laboratory.

Finally, it must be pointed ; iin that all compounds which were used contain natural boron. If B^{10} enriched substances would be used, the thicknesses of the detectors c ild be greatly decreased with a correspon ing increase in the gamma ray discrimination ch racteristics.

Acknowledgments

We thank O. Lires, L. Casas, . Isaurralde and U. Traub for technical assista ce, and Nuclear Physics Department, and Re ctors Department of the C.N.E.A. for the use o equipment.

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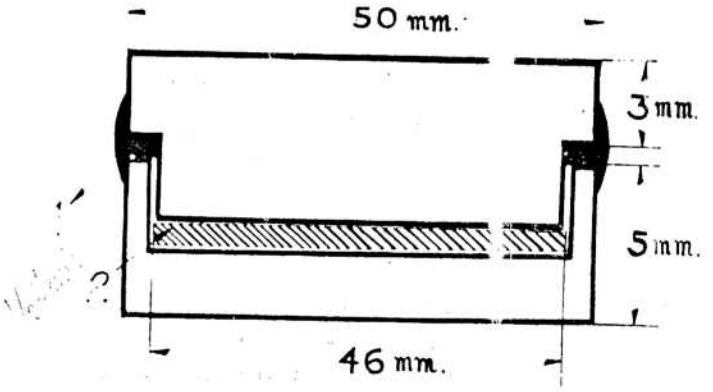


Fig. 1 - 1) Cement.
2) Solid Scintilla or Film.

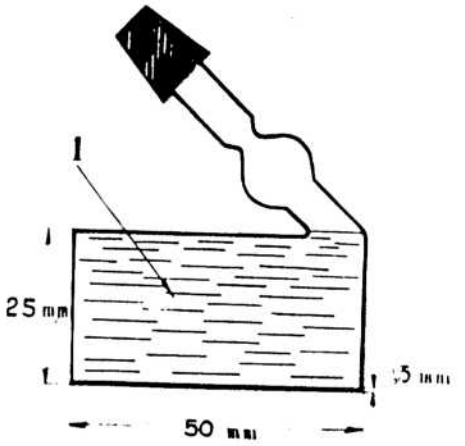


Fig. 2 - 1) Scintillator Solution.

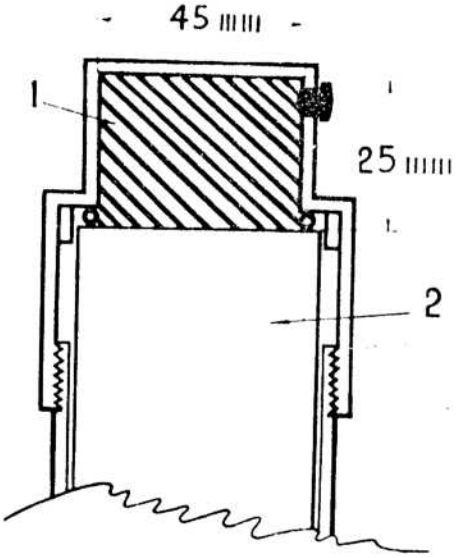


Fig. 3 - 1) Scintillator Solution.
2) Phototube.

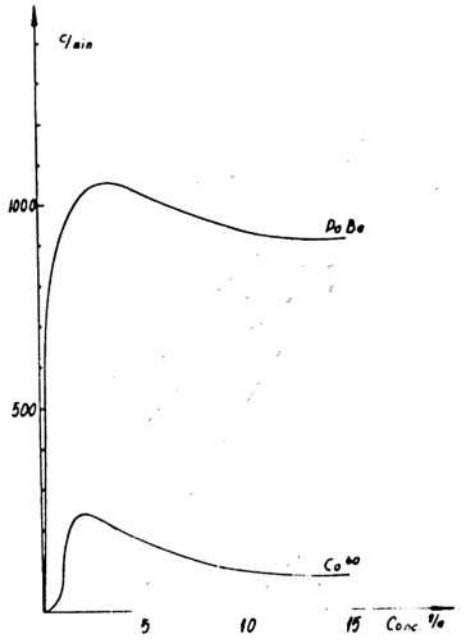


Fig. 4 - Counting rates vs. concentration in hydroxiborazaro phenanthrene solution in benzene.

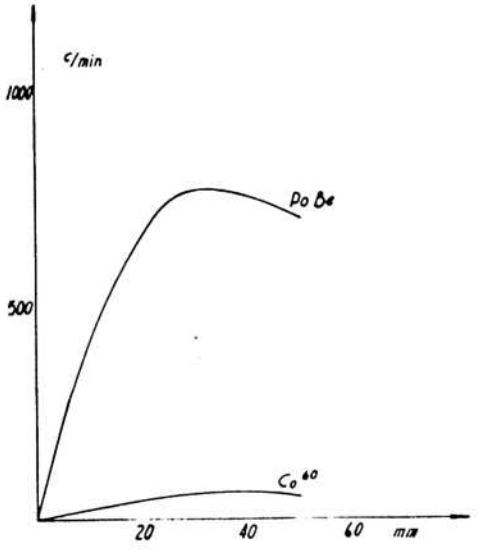


Fig. 5 - Counting rate vs. solution thickness for a solution of hydroxiborazaro phenanthrene, 4 g/l in benzene.

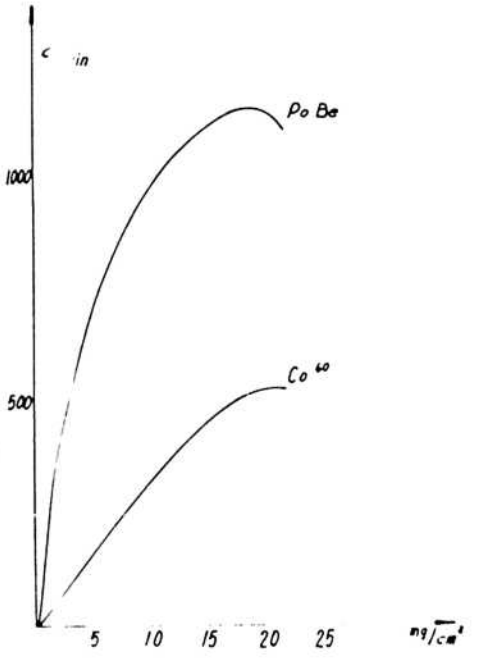
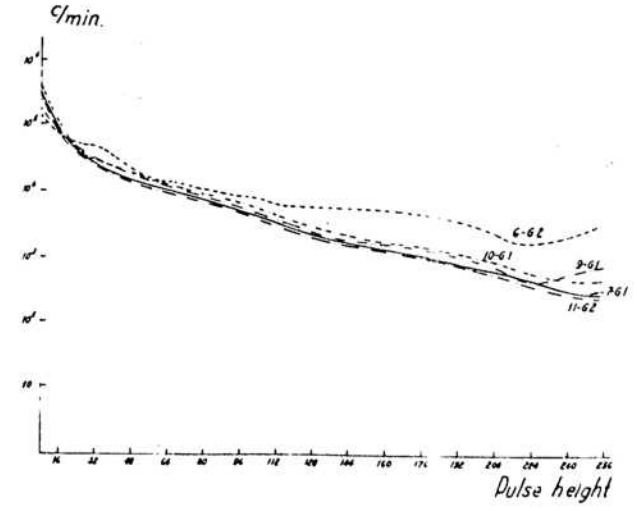
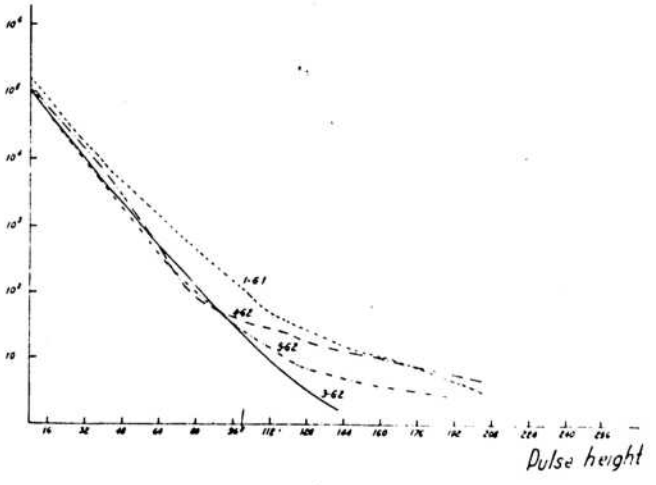


Fig. 6 - Counting rate vs. thickness of naphtyl-methyl borazine in a lucite cell.



a



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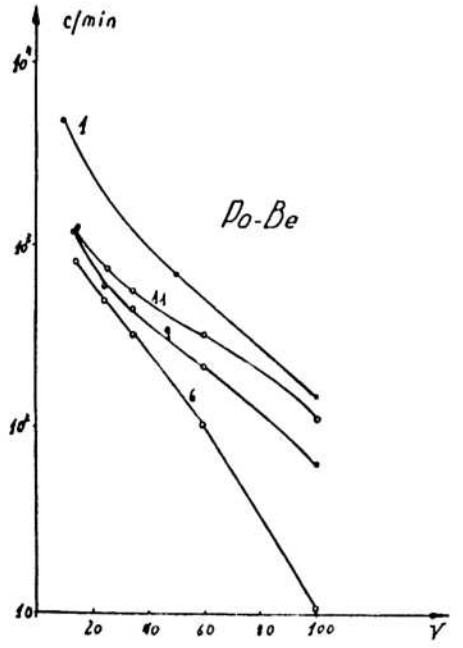

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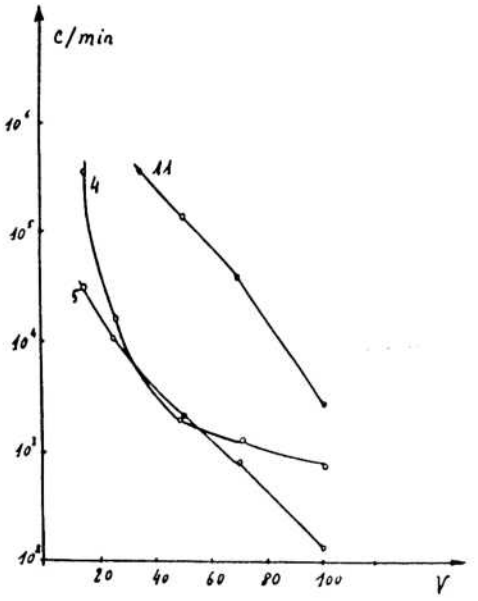

d

Fig. 7 - Typical counting curves. Numbers refer to Table
a) Liquid cells.
b) Solid films. Irradiate with Li^7 (d,n) Be^8.
c) Irradiated with Po-Be source (single channel analyzer).
d) Irradiated with the nuclear critical facility (single channel analyzer).

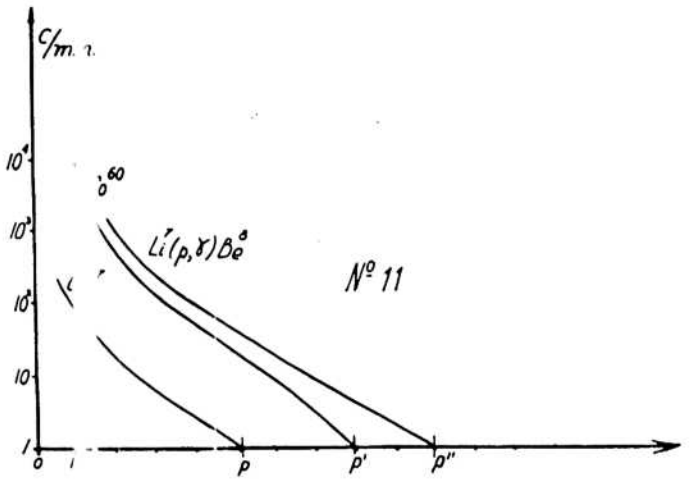

Fig. 8 - Typical gamma ray counting curves.

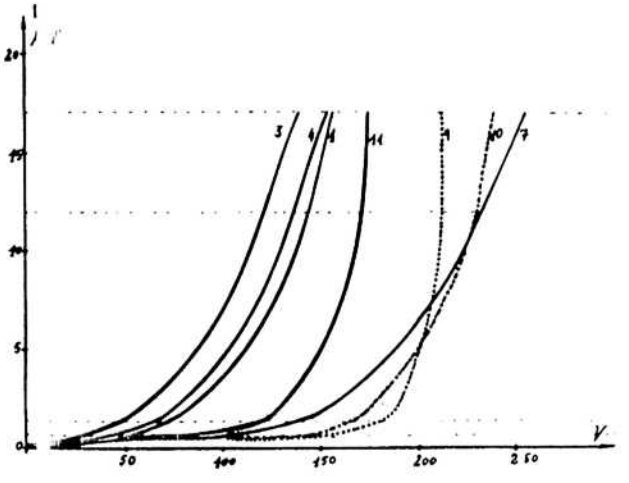

Fig. 9 - Gamma ray calibration of the scintillators. Numbers refer to Table I.

TABLE I

N°	Scintillator	Solvent	Conc. or Thickness	Total ammount	Container
1	bis-borazaro naphtyl-ether	-------	7,7mg/cm^2	140 mg	lucite
3	diphenyl-phenyl borazine	-------	9,5mg/cm^2	150 mg	lucite
4	α-naphtyl-methyl borazine	-------	8,6mg/cm^2	145 mg	lucite
5	diphenyl-methyl borazine	-------	7,7mg/cm^2	140 mg	lucite
6	hydroxiborazaro phenanthrene	benzene	4 g/l	27 ml	pyrex
7	bis-borazaro-naphtyl ether	benzene	4,3 g/l	30 ml	pyrex
9	diphenyl-phenyl borazine	benzene	4 g/l	27 ml	pyrex
10	diphenyl-methyl borazine	benzene	4 g/l	30 ml	pyrex
11	diphenyl-phenyl borazine	benzene	4,5 g/l	30 ml	pyrex

TABLE II

Detector N°	Neutron Flux n, cm^2 sec	n (x) $c/cm^2 sec$	γ (xx) c/cm^2 sec	n/γ	Efficiency $\mathcal{E}$
1	,1x10^4	1625	35	46	7,6
3	2,1x10^4	924	22	42	4,3
4	,1x10^4	1012	28	36	4,8
5	,1x10^4	965	26	37	4,5
6	1x10^4	3235	53	61	15,2
7	2x10^4	4582	49	93	6,3
9	2x10^4	5338	61	87	7,3
10	,1x10^4	2503	25	100	11,7
11	,2x10^4	2381	50	47	3,2

(x) Neutron radiation from $Li^7(d,n)Be^8$

(xx) Gamma radiation from $Li^7(p,\gamma)Be^8$

Detector N° refers to Table I.