ELSEVIER

Nuclear Instruments and Methods in Physics Research A 492 (2002) 35–42

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

www.elsevier.com/locate/nima

Radioactivity measurements of a large number of adhesives

J. Busto[a,*], Y. Gonin[a], F. Hubert[b], Ph. Hubert[b], J.-M. Vuilleumier[a]

[a] *Institut de Physique, Université de Neuchâtel, Rue A.-L. Breguet 1, CH-2000 Neuchâtel, Switzerland*

[b] *Centre d'Etudes Nucléaires de Bordeaux-Gradignan (CENBG), Domaine du Haut-Vigneau, BP 120, F-33175 Gradignan Cedex, France*

Received 7 May 2002; accepted 7 May 2002

Abstract

Low energy and low counting rate experiments in neutrino and astroparticle physics need building materials with natural radioactivity as low as possible. The intrinsic activity of a large number of adhesives, used in the low-level rate experiments MUNU, St-Gotthard and NEMO, is presented.

PACS: 29.40.Wk; 29.30.Kv

Keywords: Adhesive; Radioactivity; Ge spectrometer; Radio-isotope; Very low background experiment

1. Introduction

In the last few years there has been a growing interest in using high sensitive methods of low counting rate for solving various problems in nuclear and particle physics [1]. The most advanced progress has been made where extremely rare events have to be detected, like in solar neutrino [2], double beta decay [3] and dark matter [4] experiments. Those events being sought are so rare that the struggle to eliminate all the various sources of background noise is sine qua non for any experiment. First of all, to reduce the effects of the ever-present cosmic-rays, the physicists set up the experiment far under ground. Next, the detector should be protected against the ubiquitous natural radioactivity and this is accomplished by surrounding it by shielding. Finally, the detector itself should be built with materials countering only infinitesimal quantities of naturally occurring radioactive elements. In response to these experimental exigencies, ultra-low-background-noise gamma-ray spectrometers have been developed.

In this paper, we present the results of gamma-ray spectroscopic measurements of 37 adhesives used principally in the three low event-rate experiments MUNU [5], St-Gotthard [6] and NEMO [7]. Indeed, adhesive technology has become essential for scientists and engineers, because it covers a wide range of applications and is often easy to use and not expensive. First measurements have shown that the level of radioactivity can vary by 2 or 3 orders of magnitude from one adhesive to another. As a consequence, the knowledge of the radioactivity level of such products is crucial.

*Corresponding author. Tel.: +41-32-718-2940; fax: +41-32-718-2901.

E-mail address: jose.busto@unine.ch (J. Busto).

0168-9002/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0168-9002(02)01280-9

2. Adhesives

Assembly techniques are largely employed in the set-up of experimental devices and, in some cases, the only way to fit together different parts is to use adhesives. Instruments used in physical research are often subjected to high stress due to vibrations, extreme temperatures, peculiar environmental conditions, etc. Moreover, some elements in the set-up have specific electric properties (resistivity or conductivity, high voltage, etc.) or optical characteristics (index of refraction, spectral transmission, opaqueness to light, etc.). So, adhesives must endure the specific constraints of experiments. In addition, the choice of an adhesive is strongly linked to its viscosity and curing performances. For instance, anaerobic adhesives are single-component adhesives whose cure occurs when deprived of oxygen. They are often used as gaskets or for threadlocking. UV-cure adhesives polymerize under the action of UV-light. The curing time depends on the intensity and wavelength of the applied light. The cyanoacrylates polymerize on contact with slightly alkaline surfaces (normally moisture in the air is sufficient to set off the curing mechanism in few seconds). For the two-component adhesive group, the resin needs to be mixed with a hardener to cure.

To illustrate the use of adhesives in an experimental set-up, the calorimeter part of the NEMO 3 detector has been chosen. This calorimeter consists of 1940 low background 3″ and 5″ photomultiplier (PM) tubes coupled to plastic scintillators. Fig. 1 shows a schematic view of the mounting of a 5″ PM. All PM components (scintillators, light guides, magnetic shields, etc.) were carefully selected for their absence or very weak levels of radioactive contaminants. As shown in the figure, seven different types of adhesives were used in this device. The "Cyanolit" was used in a few local points which require very fast curing, like scintillator wrapping or optical fiber mounting. The scintillator was glued to the light guide with the optical "BC-600", which becomes very hard after curing. The optical "RTV 615" was used between the light guide and the plastic PMMA interface, and between this interface and the PM tube. After curing, this glue must stay soft, in order to be able to allow some repairs if necessary. For the light opaqueness, both the "RTV 106" (paste) and "RTV 116" (flowable) were selected. Finally, all PM devices were fixed on the copper frame of the NEMO detector using the optical "Epo-Tek 310", selected for its low viscosity and because it stays soft after curing and supports thermal shocks. Note that for direct contact of the device on the

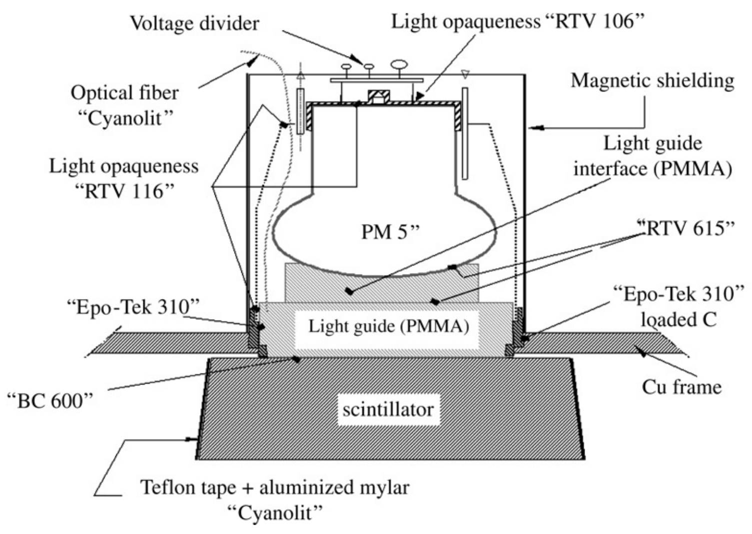

Fig. 1. Schematic view of the mounting of a photomultiplier tube showing the location of the different adhesives used.

copper frame, the glue was loaded with carbon in order to have the light opaqueness at this point. Of course, besides their mechanical or optical properties, all these adhesives were also highly selected in their radioactive contaminants (see following tables).

3. HPGe measurements

Gamma spectroscopy with germanium detectors is a powerful technique used to measure the radiopurity of materials. It has many advantages compared to other methods as, for example, to distinguish many radio-isotopes during one measurement without destruction or chemical change of the sample. This is particularly interesting for natural radioactive series, where the knowledge of disequilibria between isotopes is crucial for low-background experiments. Significant improvements were realized these last 10 years on the sensitivity of γ-spectroscopy due to development of ultra-low background cryostats, availability of large Ge crystals and use of efficient shieldings placed in underground laboratories.

4. Experimental set-up

The detectors involved in this work were all built by the French company "Eurisys Mesures". First, the materials used for cryostats were selected or specially developed for their low level or absence of radioactivity. In particular, the pipe and the cover were made from very pure Al (4%) Si alloy supplied by the Pechiney company. The activity of this Al alloy is known to be less than 0.3 ppt on U and Th. All Ge crystals were coaxial and of "p-type". Such a crystal, instead of an "n-type", allows minimizing the effect of the ^{210}Pb inner surface contamination of the endcap. It has however the disadvantage to lower the γ-efficiency at low energy.

In order to reduce the background due to cosmic-rays, the detectors were installed underground. The results presented in this work were obtained in two laboratories: (1) the "La Vue-des-Alpes" laboratory (VdA) [8], located in the Swiss Jura mountains (600 m water-equivalent), equipped with a 400 cm^3 ultra-low background spectrometer; (2) the "Laboratoire Souterrain de Modane" (LSM) [9] in the Fréjus tunnel between France and Italy (4800 m water-equivalent) where two Ge spectrometers were used (400 and 120 cm^3 crystals). The difference in depth between the two laboratories is not really significant from the point of view of background reduction for measurements presented in this work.

The detectors were shielded with 15 cm of very pure OFHC copper and 20 cm of low activity lead. In addition, this passive shielding was enclosed in a tight aluminium box pressurized with nitrogen in order to keep the radon out of the detection cell. Fig. 2 shows, as an example, the spectrometer installed in the VdA laboratory. For the Ge spectrometers in the LSM, part of the inner Cu shielding was replaced with 6 cm roman time lead.

The background spectrum measured during 28 days with the VdA spectrometer is presented in Fig. 3. The observed γ-lines are from natural radio-isotopes, essentially ^{214}Pb and ^{214}Bi from the ^{238}U family, ^{208}Tl and ^{212}Pb from the ^{232}Th series and ^{40}K, or from ^{137}Cs, a fission product isotope mainly formed during atmospheric bomb tests and the Tchernobyl nuclear accident. The e^+–e^- annihilation line at 511 keV is essentially due to the presence of residual cosmic muons and neutrons in the VdA laboratory. This gamma line is strongly reduced in the background spectra recorded in the LSM laboratory because of its greater depth.

5. Determination of the abundance of radio-isotopes

As usual, the abundance of the observed isotopes was determined by the strength of characteristic gamma-lines. ^{40}K and ^{137}Cs are identified by their well-known γ-lines (1461 and 662 keV, respectively). In the ^{238}U series, the γ-emitters are essentially ^{234}Th (63 and 93 keV), ^{234m}Pa (1001 keV), ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV). In the ^{232}Th series the measured

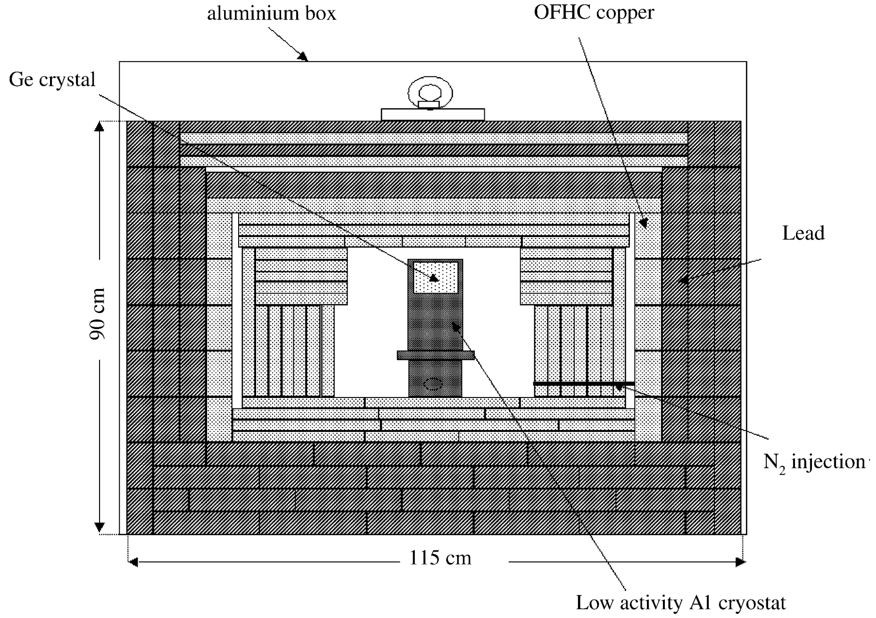

Fig. 2. Drawing of the shield and the detector installed in the VdA laboratory.

radio-isotopes are ^{228}Ac (338 and 911 keV), ^{212}Pb (238 keV) and ^{208}Tl (583 and 2614 keV).

A detailed look at the two decay chains shows that the present experimental conditions allow us to determine: (1) activity of ^{238}U (same as ^{234m}Pa and/or ^{234}Th) and ^{226}Ra (in equilibrium with ^{214}Pb and ^{214}Bi); (2) activity of ^{228}Ra equal to that of ^{228}Ac and ^{228}Th (with ^{208}Tl and ^{212}Pb decays). One must notice that ^{232}Th, head of the Th series, is not measurable in the present experimental conditions.

The activity a_{ct} of radio-isotopes was calculated as follows:

$$a_{ct} = \frac{S}{t\varepsilon IW},$$

where S is the total number of counts in the peak of interest, t the time of measurement, ε the Ge detection efficiency, I the intensity of the γ-line and W the sample mass.

Detection efficiencies of spectrometers were calculated with the GEANT3 Monte-Carlo code [10]. Typical efficiencies of Ge detectors at 1 MeV are 5% and 2% for 400 and 120 cm^3 crystals, respectively.

The sensitivity of measurements for a given radio-isotope achievable with the involved spectrometers depends essentially on the volume of the Ge, which introduces a factor $\sim$2–3 in efficiencies between 120 and 400 cm^3 crystals, the weight of samples and time of measurement and, last but not least, the activities of other isotopes in the sample itself which can complicate the analysis of the spectrum. As an example, limits in ^{238}U activity are determined by using counting rate in the 93 keV line of ^{234}Th or in the 1001 keV line of ^{234m}Pa if the low energy region becomes too much complex. Due to different branching ratios and efficiencies of detection of the two γ-lines, the calculated limit can be markedly distinct.

6. Results

Results of HPGe measurements of 37 adhesives are given in Tables 1–4. In each table, the first two columns give the characteristics of adhesives (name, distributor, essential features and applications). The following columns (3–8) present values

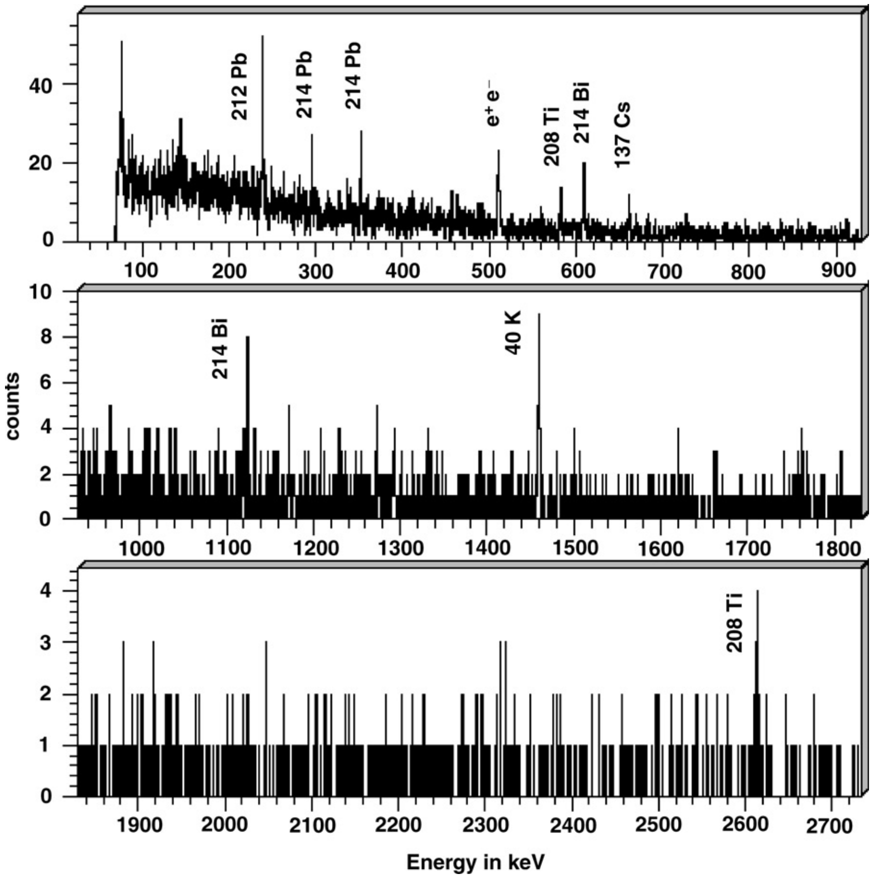

Fig. 3. Detail of the VdA Ge background spectrum (672 h).

or limits of activities in mBq/kg.[1] The indicated errors are statistical uncertainties only at the 1σ level while the limits are at the 2σ level. A systematic uncertainty of about 10% is associated with the Monte-Carlo calculations of the Ge efficiencies.

Table 1 groups nine Room Temperature Vulcanizing (RTV) silicone compounds, 8 of them being distributed by the General Electric Silicone company and the last one coming from the Rhône-Poulenc company. The most striking feature in this table is that essentially the two black paste adhesives, namely "RTV 133" and "RTV 627", present a significant level of radioactivity compared to the other RTV silicone samples.

In Table 2, measurements of eight adhesives essentially used for optical purposes are presented.[2] Most of the results in this table are limits. Only in "Epo-Tek 320", an optically opaque black adhesive, an activity of 2 Bq/kg of ^{40}K is measured.

Table 3 gives the radioactivity of fourteen two-component adhesives with different characteristics

[1] The specific activity of a given radio-isotope in a sample is also often expressed in g/g (ratio of the radio-isotope mass to the total sample mass). The relation between g/g and mBq/kg is given by

$$1\ \mathrm{g/g} = 7.554 \times 10^{-23} \times a_{\mathrm{ct}} \times A \times T_{1/2}$$

where a_{ct} is the specific activity in mBq/kg, A the mass number and $T_{1/2}$ the half-period in years.

[2] Note that the two adhesives "RTV 615" and "RTV 141", presented in Table 1, can also be used for optical purposes.

Table 1
Radioactivity measurements of RTV silicone samples

Adhesive	Key features and applications	Activity (mBq/kg)					
		^{238}U series		^{232}Th series		^{137}Cs	^{40}K
		^{238}U	^{226}Ra	^{228}Ra	^{228}Th		
RTV 106 General Electric	Red paste, high temperature Sealant	200 ± 50	<20	<15	<20	<5	250 ± 70
RTV 116 General Electric	Red, flowable, high temperature Narrow space potting	<250	<45	<70	<10	<50	<830
RTV 133 General Electric	Black paste, sealant O-ring	580 ± 280	600 ± 70	380 ± 120	400 ± 70	<35	1480 ± 320
RTV 160 General Electric	White, flowable General purpose	<170	35 ± 10	<40	<12	<17	370 ± 130
RTV 162 General Electric	White paste, bonding, insulating General purpose, O-ring	<120	33 ± 8	<50	<17	<10	370 ± 130
RTV 167 General Electric	Grey paste, high strength O-ring, sealant	<80	<30	<13	<6	<8	500 ± 80
RTV 615 General Electric	Transparent, low viscosity Optical coupling	<130	<40	<15	<20	<5	380 ± 100
RTV 627 General Electric	Black paste, sealant O-ring	<8300	1880 ± 250	1050 ± 200	1350 ± 100	<35	2650 ± 600
RTV 141 Rhône-Poulenc	Transparent, low viscosity Optical coupling	<500	<40	<70	<70	<30	1350 ± 500

Table 2
Radioactivity measurements of optical grade adhesive samples

Adhesive	Key features and applications	Activity (mBq/kg)					
		^{238}U series		^{232}Th series		^{137}Cs	^{40}K
		^{238}U	^{226}Ra	^{228}Ra	^{228}Th		
Epo-Tek 301-2FL Epoxy Technology	Optically clear, low viscosity For optical fiber	<1100	9 ± 3	<7	<60	<1.5	<25
Epo-Tek 310 Epoxy Technology	Optically clear, low viscosity Flexible, room temperature cure	<330	<15	<20	<8	<8	<110
Epo-Tek 320 Epoxy Technology	Black, optically opaque Potting	<280	<70	<80	<35	<50	2000 ± 580
Stycast 1264 Emerson & Cuming	Transparent, low viscosity Epoxy encapsulant	<220	<33	<50	<34	<22	<417
Stycast 1266 Emerson & Cuming	Optically clear, low viscosity Epoxy encapsulant	<800	27 ± 3	<16	<40	<0.9	<40
BC-600 Bicron	Clear, optical epoxy cement For plastic scintillators	<150	<42	<50	<20	<17	<235
BC-630 Bicron	Colourless Silicone optical grease	<200	<17	<50	<10	<17	<233
NE581 Nuclear Entreprise	Clear, optical epoxy cement For plastic scintillators	<300	<25	<117	<15	<12	<233

Table 3
Radioactivity measurements of two-component adhesive samples

Adhesive	Key features and applications	Activity (mBq/kg)					
		^{238}U series		^{232}Th series		^{137}Cs	^{40}K
		^{238}U	^{226}Ra	^{228}Ra	^{228}Th		
Scotch-Weld 2216 3M	Gray Great flexibility	13000 ± 1000	8300 ± 30	14560 ± 60	19510 ± 90	<1	14300 ± 200
EA 9321—Hysol Henkel	Gray Wide range of temperature	1500 ± 300	19 ± 3	99 ± 7	25 ± 6	<1	240 ± 30
EA 9361—Hysol Henkel	Gray Cryogenic bonding	1600 ± 700	1480 ± 40	2770 ± 70	3530 ± 79	<30	1700 ± 200
EA 9394—Hysol Henkel	Gray Bonding up to 175°C	11000 ± 2000	40 ± 10	370 ± 30	<490	<5	170 ± 90
Tra-Bond 2130 Tra-Con	Transparent Sealant	<17000	470 ± 80	580 ± 210	<900	<200	1400 ± 700
Tra-Bond 2151 Tra-Con	Blue paste Good thermal conductivity	4700 ± 3300	270 ± 40	240 ± 60	270 ± 70	<30	<200
Stycast 2850FT Emerson & Cuming	Black or blue liquid, encapsulating Thermally conductive	2800 ± 500	160 ± 10	510 ± 20	1170 ± 30	<15	150 ± 40
Eccobond 285 Emerson & Cuming	Black General purpose	1000 ± 400	291 ± 7	100 ± 10	<320	<8	100 ± 40
Loctite 3295 Henkel	Green paste General purpose	<5000	280 ± 20	<90	<210	<34	970 ± 190
Araldite 2011 Vantico	Pale yellow paste General purpose	<35	<20	<8	<3	<3	<84
Araldite 2015 Vantico	Beige paste Composite materials, metals	<10000	4000 ± 60	290 ± 50	230 ± 30	<60	78000 ± 1270
Araldite 2020 Vantico	Transparent, flowable Glass, ceramics	<250	<17	<33	<15	<17	<133
Epon 828 Shell	Beige paste General purpose	<1800	<8	<22	<60	<9	<33
Epo-Tek 417F Epoxy Technology	Thick silver paste Electrically conductive	<2500	68 ± 11	<52	<131	<18	<65

and applications. The most active adhesive is the "Scotch-Weld 2216" (first position), "Araldite 2015" being the most active in ^{40}K (78 000 mBq/kg).

Table 4 gives the radioactivity of six single-component adhesives also with characteristics and applications. Except the "7031" from General Electric, these adhesives have a cyanoacrylate base.

Upon inspection of the whole data, it appears that the tested adhesives have not been contaminated with ^{137}Cs, in the limit of the experimental sensitivity which has a mean value of 25 mBq/kg. Note that the activity of ^{40}K is strongly different from one sample to another, ranging from $\sim$78 000 to $\sim$25 mBq/kg. The interpretation of these differences between samples is not straightforward because the chemical products and origins of raw materials entering in the composition of adhesives are generally not known.

Finally, as far as equilibrium in radioactive chains are concerned, the comparison between activities of the two feeders (^{238}U and ^{226}Ra for the U series, ^{228}Ra and ^{228}Th for the Th series) shows that there is no general behavior. For example, in "Hysol EA 9361" (Table 3), all isotopes in the U family are in equilibrium, while in the other two Hysol adhesives, "EA 9321" and "EA 9394", one observes a strong disequilibrium. Such results must be taken into account when one chooses an

Table 4
Radioactivity measurements of single-component adhesive samples

Adhesive	Key features and applications	Activity (mBq/kg)					
		^{238}U series		^{232}Th series		^{137}Cs	^{40}K
		^{238}U	^{226}Ra	^{228}Ra	^{228}Th		
Loctite 401 Henkel	Colourless General purpose	<6600	110 ± 20	<160	<360	<52	<740
Loctite 480 Henkel	Black Metal to metal	<2700	210 ± 30	<20	<450	<49	<180
Cyanolit 201 3M	Colourless, flowable General purpose	<7000	250 ± 30	<33	<520	<12	<200
Cyanolit 241 3M	Colourless, flowable General purpose	<14000	800 ± 70	180 ± 100	<831	<120	<1500
Cementit CA-12 Merz & Benteli	Transparent Synthetic material	<7000	<28	<150	<450	<7	<230
7031 General Electric	Clear insulating varnish Cryogenic temperatures	<2900	49 ± 8	<10	<110	<3	370 ± 100

adhesive to be used in an ultra-low background experiment where specific radio-nuclides are strongly forbidden. It is also interesting to note that "Epo-Tek 417F", a high-conductivity glue, has quite a low activity despite the presence of a large amount of silver in it, often polluted with U and Th.

7. Conclusions

Adhesives are currently used in the set-up of various apparatus and are sometimes the only possibility to adjust correctly an experimental device. Moreover, in the field of nuclear and particle physics, ultra-low background experiments have to eliminate as far as possible all sources of spurious events due to the presence of natural radioactivity in the materials used to build the detector. Consequently, the use of adhesives must also be free of radioactive contamination. Through low-background high-purity germanium spectrometer studies, the radioactivity of a large number of adhesives to be utilized in the low-level rate experiments MUNU, St-Gotthard and NEMO, has been controlled. The results show strong variations in the measured values from one adhesive to another. In this paper, the radioactivity of 37 adhesives has been given together with their characteristics.

Acknowledgements

The authors would like to thank D. Schenker who helped setting up the mixing machine, A. Guiral and F. Mesples-Carrère who worked on the photomultipliers of the NEMO experiment. One of the authors (YG) would also like to gratefully acknowledge D. Gerber for his constantly wise advice and D. Gritti for enlightening discussions.

References

[1] G. Heusser, Ann. Rev. Nucl. Part. Sci. 45 (1995) 543.
[2] T.A. Kirsten, Nucl. Phys. B 87 (2000) 152.
[3] M. Moe, P. Vogel, Ann. Rev. Nucl. Part. Sci. 44 (1994) 247.
[4] L. Bergström, Rep. Prog. Phys. 63 (2000) 793.
[5] C. Amsler, et al., Nucl. Inst. and Meth. A 396 (1997) 115.
[6] R. Luescher, et al., Phys. Lett. B 434 (1998) 407.
[7] F. Piquemal, et al., Nucl. Phys. B 77 (1999) 352.
[8] The "Vue-des-Alpes" underground laboratory on the web: http://www.unine.ch/phys/corpus/VdA/VdA.html.
[9] The "Laboratoire Souterrain de Modane" on the web: http://www-lsm.in2p3.fr.
[10] R. Brun, et al., GEANT, CERN Program Library.