Low-level germanium gamma-ray spectrometry at the μBq/kg level and future developments towards higher sensitivity

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Abstract. GeMPI, a highly sensitive germanium gamma spectrometer operated at the Gran Sasso underground laboratory is described. Its complete cryostat system and shield was made from highly selected low activity materials. Radon suppression, also during sample insertion is achieved by an air-lock system combined with an airtight steel casing around the shield, which is pressurised with nitrogen gas. The achieved background level in combination with a large sample capacity of up to 15 l around the 2.2 kg Ge-crystal allows measuring concentrations of the gamma active chain members down to 10^{-12} g/g of U/Th equivalent (12.3 μBq/kg ^{238}U, 4.06 μBq/kg ^{232}Th) and 10^{-9} g/g of K (31 μBq/kg ^{40}K). This is demonstrated with some key measurements of shielding materials as Cu and Pb. Cosmogenic production rates for 8 radioisotopes have been determined in exposed Cu as to range from 50 μBq/kg for ^{46}Sc to 2.1 mBq/kg for ^{60}Co. A possible further background reduction in Ge-spectrometry by operating naked crystals in liquid nitrogen is discussed.

1. Introduction

A Ge-spectrometer (called GeMPI) designed for measurements at the μBq/kg level sensitivity level is operated at the underground laboratory LNGS (Laboratori Nazionali del Gran Sasso) near L'Aquila/Italy since 1997. First preliminary results of background and sample measurements have been published in [1]. Primarily the spectrometer is used for material screening (radio-purity) measurements in connection with the solar neutrino experiment BOREXINO [2,3] and more recently for the double beta decay experiment GERDA [4]. Its high sensitivity makes the spectrometer also very well suited for environmental studies, as e.g. in measurements of activation products from accidental neutron exposures [5]. Special attention in the construction of the spectrometer was devoted to achieve low background rates at the lines of the primordial decay chains ^{238}U and ^{232}Th and of ^{40}K, the most prominent contaminants.

The BOREXINO experiment [2, 3] aims to measure low energy solar neutrinos in real time by elastic neutrino-electron scattering. The mono-energetic neutrinos from ^{7}Be at 862 keV are of most interest. The experiment, located also in LNGS will use 300 t of liquid scintillator to detect the scattered electrons. Since they are practically indistinguishable from other ionising events produced by natural radioactivity at the same energy, extremely high radio-purity standards must be met to detect the very low rate of a few tens of events per day in the 100 t fiducial volume. For example, the central liquid scintillator needs to contain less than about 10 nBq/kg of the U/Th decay-chain activities and about 0.3 nBq/kg of ^{40}K. The radio-purity requirements of the neighbouring construction materials are relaxed by 3 to 6 orders of magnitude, depending on their location within the detector. This corresponds to the sensitivity range of the spectrometer under discussion and also partly of other low-level Ge-spectrometers [3]. Since the tolerable contamination level at these locations is defined by γ-activity, Ge-spectroscopy is the ideal screening tool. In case of the natural decay chains interest is focused on the most gamma active progenies ^{214}Pb/^{214}Bi (^{238}U-chain) and ^{228}Ac, ^{212}Pb/^{212}Bi, ^{208}Tl (^{232}Th-chain). The high resolution spectroscopy with its spectral information gives Ge-spectroscopy an almost visualising ability and is thus superior to other screening

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methods which measure only atomic concentrations as e.g. in mass spectrometry, atomic adsorption, x-ray excitation or neutron activation. Concerning the U/Th decay chains, these techniques are only applicable to the parent nuclides, which are rarely in equilibrium with their gamma active progenies in chemically processed construction materials. Moreover Ge-spectroscopy is able, within certain limits, to observe deviations from secular equilibrium in the U/Th series. This is important, e.g. in the case of the ^{228}Ra/^{228}Th sub-chain, where the time for noticeable changes in activity ratios can occur within the lifetime of an experiment. In addition the measurement can mostly be performed in a non-destructive way without labour intensive sample pre-treatment.

The ^{76}Ge double beta decay experiment GERDA [4] will use almost bare Ge-crystals immersed in liquid nitrogen or liquid argon. Germanium is enriched in the ββ active 76 and thus the source and the detector are the same device. The highly radio-pure cryogenic liquid serves as the innermost shield against external radiation and as coolant (first proposed in [6]). Compared to conventional detector mountings with several cladding layers, which carry surface and bulk contamination, very little material is needed to hold and contact the crystals. Together with other suppression methods a background reduction of two to three orders of magnitude seems possible in comparison to the presently most sensitive ^{76}Ge double beta decay experiment Heidelberg-Moscow (HDM) [7]. However, even with material savings by almost four orders of magnitude in mass, radio-purity in the μBq/kg range will be required to reach the envisioned background. Consequently, material screening at least at the GeMPI level will be needed.

2. The low-level Ge-spectrometer GeMPI

2.1 Design criteria

Experience collected with earlier Ge-spectrometer systems [8] and with the detectors of the HDM experiment [7] resulted in the following design criteria for the construction of GeMPI:

A – Ge-crystal

minimize cosmic ray exposure by fast processing after zone refining and by surface transportation and by shielding under several meter of water equivalent whenever feasible.
crystal size optimised for high counting efficiency in Marinelli type geometry

B – Cryostat system next to the crystal

made only from screened materials with a radio-purity level below the mBq/kg level,
where possible use of NOSV grade copper[1], stored underground (minimum 15 m w.e.) shortly after electrolysis and between machining steps

electron beam welding, no soldering, crimping of contacts, metal sealing for joints

electro-polishing of metals respectively acid cleaning of all parts under clean room conditions

assembly of detector under clean room conditions

[1] copper of 99.9975 % purity, produced by Norddeutsche Affinerie, Hamburg, Germany

C – Shield

large sample volume around detector for high sensitivity of specific activity

innermost layer copper (same as above), acid cleaned, then lead with 6 Bq/kg ^{210}Pb (acid cleaned) and subsequent Pb layers with increasing ^{210}Pb-concentration
fully airtight steel box around shield, pressurised with nitrogen gas for protection against Rn

air lock system for sample insertion to keep Rn and particulate contamination out

storage space in box to allow the decay of plated out Rn progeny of Rn itself (dissolved or adsorbed) before the sample is placed into the measuring position

insertion possibility for calibration sources

2.2 The cryostat system

The concept of the cryostat system was elaborated in close collaboration with Canberra Semiconductors N.V., Olen, Belgium. FIG. 1 depicts a cross section of the found solution.

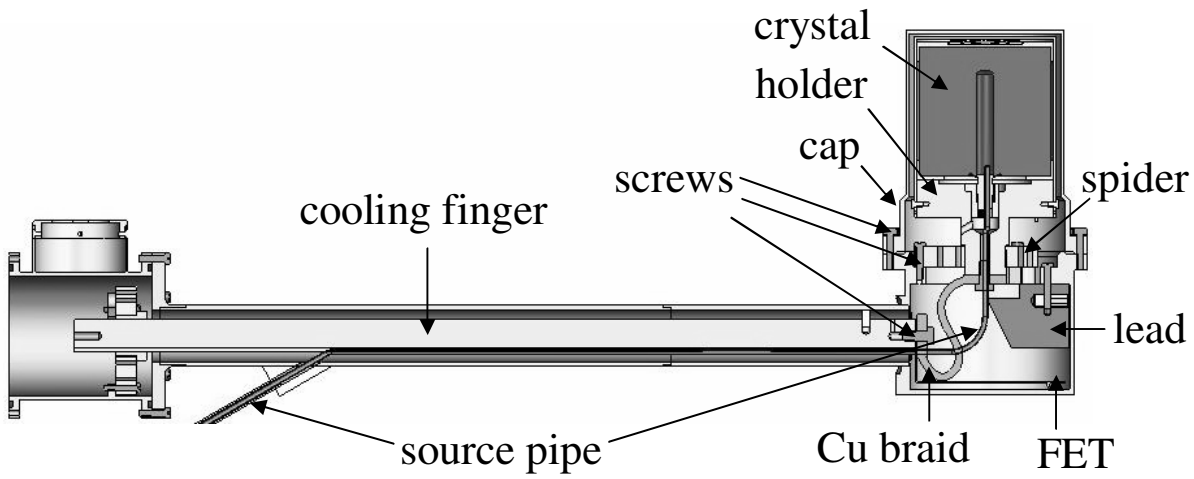

FIG. 1 Cross-section of the cryostat of GeMPI.

In the U-type mounting the isolating vacuum is common to the dewar (left to FIG. 1, not shown) and the cryostat. Normally it is maintained by molecular sieve as pumping adsorbent embedded in aluminised Mylar foil next to the cool inner wall of the dewar. In our case the Ra-rich molecular sieve was replaced by low ^{226}Ra charcoal made of coconut shells. The reason for this precaution is, that in temperature cycles, the crystal and its holder stays longer cool during the warming up phase than the rest of the system, so that ^{222}Rn emanated from the warmed up adsorbent might freeze out onto the cool parts and thus concentrates the final decay product ^{210}Pb close to or on the crystal.
On the left side of Fig.1 the crystal is mounted in an insulation can made from VESPEL® surrounded by a holder made from Cu. Also the part which fixes the holder to the warm part of the cryostat, normally called spider, as well as the insulation around the signal contact is made from VESPEL®. The Field Effect Transistor (FET) part of the electronic (provided by

Canberra) is mounted on a thin Cu plate (connected to the cool-finger) underneath a piece of low activity lead (< 0.2 mBq/kg ^{210}Pb[2]). The lead shields the residual activity of the FET unit against the crystal, although the FET, the hardpaper-baseplate and all other parts of this unit have been checked in larger quantities to assure their radioactivity being below 10 mBq/kg. Only here a special solder made from low activity lead was used in combination with a special selected flux liquid - much lower in potassium than the normally used colophon, whereas all other wire-connections are crimped with Cu sleeves. The screws indicated on the right side are made out of steel originating from a First World War battle ship. A later measurement with the higher sensitivity of GeMPI disclosed a ^{226}Ra and ^{228}Th contamination of 150 μBq/kg and 460 μBq/kg of that steel in contrast to upper limit findings prior to GeMPI construction (see also section 3.3). The Cu cover cap around the holder is sealed to the bottom part by a lead O-ring made from the same low activity lead as above.
All parts of the cryostat (shown in FIG. 1) have been machined at the workshop of the MPI-K under great care to avoid cross contamination. Electron beam welding was applied to form the lower left part of the cryostat from single pieces and to connect it to the tube around the cooling finger. This tube, the cooling finger as well as all other Cu parts, around the crystal (except the braid[3] connecting the cooling finger and the holder) have been fabricated from a special order of NOSV grade copper (99.9975 % purity, from Norddeutsche Affinerie; Hamburg, Germany). Within a few days after the electrolysis this copper was processed (melted, cast and warm formed) and placed underground, first in a former ice cave of a brewery at Heidelberg and later in the low-level laboratory of the MPI-K. The latter is covered by about 15 m w.e. concrete and rock soil which is estimated to reduce cosmogenic activation via spallation reactions by roughly a factor 20. Also during the machining phase the Cu was placed underground during longer breaks.
The hot forming by forging or rolling converts the coarse crystalline structure of the cast Cu in a much finer, less porous structure with a density of up to 8.92 g/cm^3 (about 8.7 g/cm^3 before). Thus the material becomes better suited for delicate mechanical machining, for high vacuum applications and also for acid cleaning. Acid that enters into pores of the cast material is difficult to remove. If in addition the acid solution is not radio-pure, as e.g. in electro-polishing solutions, contamination may result from residues remaining in the pores.
The finished parts of the cryostat have been cleaned (acid/deionised H_2O/alcohol) at the MPI-K in a clean room hood (class 100) and the components from copper were electro-polished with subsequent ultrasonic cleaning, passivation and clean room packing at a company[4]. The assembly of the cryostat was performed at Canberra Olen under clean room conditions. The p-type high purity germanium crystal provided by Canberra was shipped before from the United States to Belgium via boat in order to minimise cosmogenic activation. Only after the conversion to a diode (2.2 kg active volume, Ø 77.5 mm x 88.5 mm, relative efficiency 102 %) and successful testing in a test cryostat at Olen, the direct cladding parts, insulation can and holder, were machined at Heidelberg to match the size. During the production phase of the low-level cryostat the crystal was placed underground in HADES[5], close to Olen. Immediately after the transfer of that crystal into its final cryostat system and the positive performance test, the detector was transported to the low-level laboratory at Heidelberg.
Here first background tests were performed in a provisional shield made of 15 cm lead and one large cosmic veto detector (multiwire proportional chamber) placed on top. The measured background spectrum is shown below (section.3.1) in comparison with the starting background obtained at the much deeper Gran Sasso laboratory. Calibration measurements of

[2] analysed by M. Wojcik, Institute of Physics, Jagellonian University, Cracow, Poland
[3] small piece taken from a large roll screened to be radio-pure
[4] GCE-Druva, Eppelheim, Germany
[5] Underground Research Facility (URF) operated by SCK/CEN Nuclear Research centre at Mol, Belgium

the spectrometer have been carried out with various sources under different geometry and the detector was scanned horizontally and axially with collimated sources to create a data base for Monte Carlo simulations [9, 10] based on the code GEANT 3.21 (CERN Program Library).

2.3 The shield and radon protection system

In FIG. 2 different views of the GeMPI spectrometer are shown. The shield consists (from inside) of 5 cm NOSV Cu, 5 cm of Pb with 6 Bq/kg ^{210}Pb[6], 10 cm Pb with about 20 Bq/kg ^{210}Pb[7] and 5 cm Pb with about 130 Bq/kg ^{210}Pb[7]. The shield rests on a 5 cm thick slap of borated (10 % by weight) polyethylene, to keep the option for completing a neutron shield by later addition of plates on the other sides.

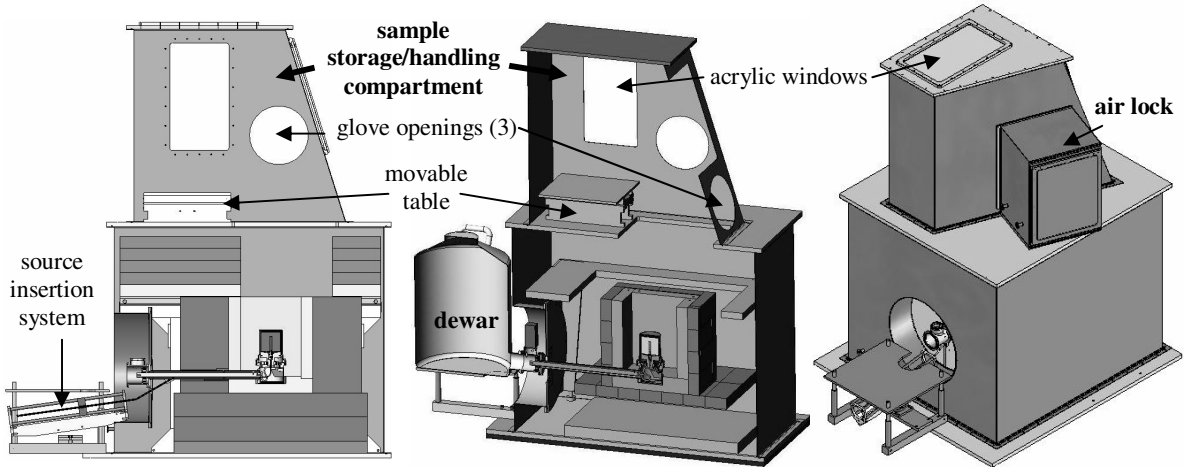

FIG. 2: Cross-sections and outside views of the GeMPI spectrometer (see text)

The top shield layers of Cu and Pb, with the same sequence, are vertically split into two asymmetric halves which can be moved sideways by the aid of slide bearings along the frame, indicated in the middle picture, so that the full sample chamber (effective space - 250x250x238 mm^3 minus Ø 94 x 106 mm detector space) is accessible from above.
A vacuum tight steel casing encloses the shield as part of the radon protection system. The other part is the (trapezoidal) sample storage/handling compartment mounted on top with the air lock box connected to it. This box has two doors. Samples to be measured are first placed inside the air lock box with the inner door still closed. Next the volume between the two doors is flushed with nitrogen gas, then the inner door is opened by the aid of gloves (round openings) from inside the sample storage/handling compartment and the sample is placed on a movable table. There is also such a table in the air lock box which can be moved through the opened inner door into the glove box compartment to transfer heavy loads. Here a small pulley can lift the sample to place it either on the inner table or to lower it into the sample chamber.
Normally the sample rests in the low Rn nitrogen gas of the glove box until the plated out ^{222}Rn and ^{220}Rn progenies or attached/dissolved ^{222}Rn have decayed, before the two top Cu/Pb lids are slid aside and the sample is replaced against the former one. Experience teaches us that this is important to assure the peak count rates of ^{214}Pb/^{214}Bi respectively of ^{212}Pb/^{208}Tl

[6] PLOMBUM, Cracow, Poland
[7] measured by W. Kolb, PTB Braunschweig, Germany (1987)

with their high γ-abundance being interpreted as ^{226}Ra respectively ^{228}Th concentrations. Moreover, the precious counting time is thus more effectively used.
The whole Rn protection system is continuously flushed at slight over-pressure with nitrogen gas from standard 50 l gas cylinders. It is directed into the sample chamber below the detector through a thin Teflon tube, so that the outward directed flow prevents Rn from diffusing in. The system with all its joints is sealed by the aid of O-ring material made from polyurethane, which was tested to have a low permeability for Rn [11] as well as a low Rn emanation rate [12]. For the gloves butyl rubber was chosen for the same reasons. However, due to their large area and small thickness additional measures had been taken to keep Rn permeation into the sample area low. When not in use the gloves are pulled back into their fixing tube and both ends of that tube are closed by lids with O-ring sealing. A valve mounted on the outer lid avoids overpressure built up during the closing procedure. The two lids strongly reduce the direct airborne Rn transfer by permeation through the glove material, but also help to minimise the accumulation of Rn between the glove and the inner lid, which at the moment of the next opening is released into the interior N_2 atmosphere.
There are two possibilities to insert calibration sources. The main one uses a 1 mm diameter encapsulated ^{152}Eu source welded to a flexible wire, with which it can be pushed through a thin Teflon tube near to the detector bottom. A motor driven spinning wheel outside the shield carries the source between the calibration position and the outside-shielded position. For Rn protection the end of the Teflon tube is closed and the box of the spinning machine can be flushed with N_2. The other (Fig.2 - source insertion system) uses a combination of a strong well type magnet and a thin counter rod magnet fixed to a flexible wire carrying a ^{55}Fe/^{133}Ba source. They are separated by a Cu/Teflon tube, which forms an extension of the cryostat tube (Fig.1 - source pipe). The Teflon tube guides the source along the cool finger through the signal contact into the well of the crystal. Here the almost wall-less p-contact surface allows extending the calibration energy range into the X-ray regime. Unfortunately the latter method turned out to be unpractical since the stiffness of the Teflon tube turned out to be much higher at low temperature than at room temperature during the final function test before the cryostat assembly was completed. The risk that the source gets blocked in the bend part of the tube under the crystal holder does not allow pushing it across this point.

3 Measurements

3.1 Background measurements

After a few months of testing at the low-level laboratory at Heidelberg, the shield was disassembled and GeMPI (FIG. 2) was installed [10] at the low background counting facility[8] of the Gran Sasso underground laboratory LNGS. At this occasion all parts have been cleaned once more. Already at Heidelberg the heavy Cu plates of the inner chamber have been washed with diluted nitric acid, rinsed with distilled water and packed for shipping. The lead bricks were cleaned directly before installation, those for the inner layers with a mixture of acetic acid/H_2O_2 and deionized water, the outer ones with alcohol. Clean room clothing was obligatory during the set-up phase of GeMPI.
The about 3800 m w. e. rock shielding above the laboratory reduces the muons flux by 6 orders of magnitude compared to sea level, so that the muonic contribution to the background should be negligible compared to Heidelberg, where only about a factor of 3 is effective by the 15 m w. e. overburden. The integral background rate was immediately lower by more than two orders of magnitude compared to Heidelberg and continuously decreased with time due to the decay of cosmogenic radionuclides, mainly ^{57}Co, ^{58}Co in Cu and Ge, ^{65}Zn in Ge. After

[8] C. Arpesella is thanked for help and for hosting GeMPI at the facility under her responsibility during the installation phase

about 2 years it slowly leveled off to about 0.04 cpm (100 – 2730 keV), roughly 2 to 3 times lower than at start. This factor would have been much larger without all the shielding measures before the cryostat assembly and the preconditioning at Heidelberg. In FIG. 3 spectra are compared which have been measured at Heidelberg unshielded and with the provisional shielded of about 15 cm Pb and one veto detector on top and at Gran Sasso with the full shield. The latter background spectrum represents only a rather weak statistic of about 60 d counting time, collected between sample measurements during the first 1.5 years of operation at LNGS. A reduction of about 5 orders of magnitude compared to the unshielded mode at Heidelberg seems to be almost independent on energy, at least up to the Compton edge of the 2.615 MeV ^{208}Tl line. The shielded measurements at Heidelberg and at Gran Sasso differ by more than two orders of magnitude. A short unshielded measurement at Gran Sasso yielded a comparable continuous level as at Heidelberg, only lower by factors 2 to 5 depending on energy. This is mainly due to a lower concentration of primordial radionuclides at LNGS and less to the difference in muon flux. The contribution of muons to the total unshielded count rate of 8100 cpm (100-2690 KeV) at Heidelberg is below 1%.

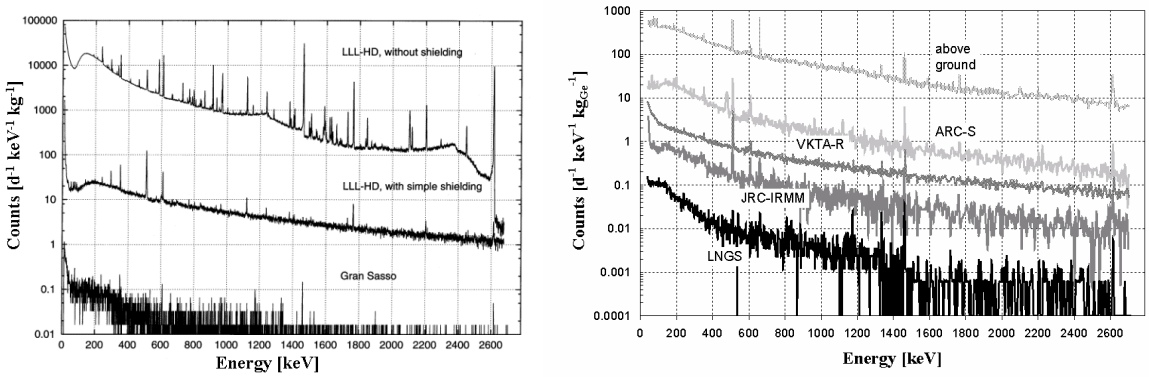

FIG. 3 Background spectra of GeMPI at Heidelberg and Gran Sasso (left) and in comparison with other detectors from CELLAR[9] laboratories (right), taken from [13]

On the right part of FIG. 3 the GeMPI background (lowest spectrum, this time with 101 d statistic, collected after about 3 years at LNGS) is compared with the background of (shielded) low level detectors from other European underground laboratories [13] co-operating in CELLAR[9].

The overburden of this laboratories varies from almost zero (ARC-S and upper spectrum), 110 m w. e. (VKTA-R), 500 m w. e.(JRC-IRMM) to 3800 m w. e. (LNGS). In [13] it is recognized that the normalized integral counting rate of the shown spectra decreases only up to about 500 m w. e. in accordance with the growing overburden and than levels off. Consequently, the background contribution from residual contamination becomes dominant in relation to that of cosmic muons beyond that depth. This also holds for GeMPI, but the difference in FIG. 3 reflects the higher radio-purity that has been achieved with GeMPI.

In Table I background information is given for the most abundant lines of the primordial decay chains U/Th, of ^{40}K and of ^{137}Cs (antropogenic), ^{60}Co (cosmogenic) as well as the integrated background between 100 and 2730 keV. For GeMPI they have been evaluated from a measuring time of 101 days. They are compared with those measured in the individual detectors of HDM [14, 15], representing together a statistic of close to 50 kg y and thus with the highest statistic ever measured in low-level Ge-spectroscopy. Also here an improvement is

[9] Collaboration of European Low-level Underground Laboratories, see e.g. www.ptb.de/org/6/63/udo/cellar.html

recognized at least for the ^{226}Ra sub-chain lines. The count rates for ^{40}K, ^{60}Co and ^{137}Cs are comparable to those of the cleanest HDM detectors. The difference in the total background count rate between GeMPI and the HDM detectors may partially reflect the higher contribution from the two neutrino ßß-decay of the isotope ^{76}Ge, which is higher enriched in the HDM detectors (~68 % versus 7.44 % in natural Ge-detectors like GeMPI). On the other side the HDM experiment had a complete neutron shield around detectors # 1 2 3 5 and a cosmic veto shield for all detectors. However, the latter resulted in a reduction of only about 0.5 % [16] and the effect of the neutron shield was estimated to be also only in the sub % range [17].

Table I: Background count rates for the main primordial lines, for ^{40}K, ^{137}Cs, ^{60}Co and integrated over the energy range 100 - 2730 keV for GeMPI and the HDM detectors (line background from [14], integral from [15]).

		peak (integral) background count rate [kg^{-1} y^{-1}]	
energy [keV]	chain/nuclide	GeMPI	HD-M detectors 1-5
352	^{238}U/^{214}Pb	≤ 24	112 – 177
609	^{238}U/^{214}Bi	≤ 25	90 – 137
583	^{232}Th/^{208}Tl	≤ 21	18 – 42
2615	^{232}Th/^{208}Tl	18 ± 5	11 – 22
1461	^{40}K	86 ± 12	74 – 291
662	^{137}Cs	57 ± 27	41 – 914
1173	^{60}Co	43 ± 10	46 – 71
1332	^{60}Co	35 ± 8	36 – 54
100 – 2730		6840 ± 110	11400 – 18700

3.2 Choice of optimal sample size

The units applied so far - counts (kg keV y)$^{-1}$ and counts (kg y)$^{-1}$ - are useful for background comparisons. More relevant for the sensitivity in Ge-spectroscopy is the specific activity A [Bq/kg] that can be detected after a certain measuring time. Besides the background B (average from both sides of the peak) it takes into account the counting efficiency ε_M for the sample with the mass M. In first approximation, by neglecting any proportional factors it can be expressed as:

$A \approx B^{1/2} (\varepsilon_M M t)^{-1}$, if the peak background is zero
$A \approx (B + t b + t^2 \sigma^2_b)^{1/2} (\varepsilon_M M t)^{-1}$, if the peak background rate b is not negligible
with:
ε_M = efficiency for the sample with the mass M
t = measuring time of the sample
σ_b = statistical error of the peak background rate, see e.g. Table 1.

The product ε_M M increases until self-adsorption within the sample becomes dominant. Some orientation is available from the 1/e thickness for the highest energy of interest, in our case the 2.615 MeV line of ^{208}Tl. For example, it is 234 mm; 33.4 mm, 29.6 mm; 20.7 mm for water, iron, copper, lead respectively. With this information and economic considerations we have designed the minimal distance between the detector and the inner Cu wall to be about 78 mm

on the sides and 132 mm on top (238 mm maximal sample height aside from the detector). The Marinelli type geometry results in an effective volume of close to 15 l since the detector-cap is cylindrical and the sample chamber quadratic in cross section. If affordable, the sample chamber is always completely filled, even though the gain in sensitivity for dense materials like Pb is only minor, but the reliability for the background correction in data evaluation is higher. Uncertainties of minor background differences between the empty and the full chamber, not only from higher radio-impurities in the chamber wall, but also from Rn concentration variations[10] in the nitrogen purging gas are thus minimised. For GeMPI extensive background measurements showed indication of this problems but the statistic significance is of course always limited to a few %.

3.3 Some key sample measurements

Copper, lead, iron, and Teflon® are very common materials used for shielding or construction of rare event rate detectors in neutrino, double beta, and in dark matter experiments. Measurements of these materials performed with GeMPI resulted in the data given in Table II.

For the Low Background Facility of the LENS solar neutrino experiment [19] Cu was used as inner shielding material. Cosmic activation could be kept low by a close co-ordination of the Cu producer, the company to roll it and that of the final machining. Out of this production line two sets of Cu plates (33 mm thick) have been prepared to fit into the sample chamber of GeMPI. Old ships iron of a First World War battle ship was used since many years for different purpose of low-level projects including the fabrication of the screws for the HDM detectors and for GeMPI (FIG. 1). A roll of stainless steel foil (0.125 mm thick) was purchased in course of emanation studies for the BOREXINO experiment. Two lead samples (of DowRun- and Boliden quality according to the supplier J L Goslar) have been investigated for the GERDA experiment [4] and one lead sample made from ancient roman lead [20] for the cryogenic double beta decay experiment CUORE [21]. The roman lead was measured in form of two open-end cylinders and a top plate (1^{st} cylinder: Øi=106mm; Øa=159mm; h=76.5mm; 2^{nd} cylinder: Øi=106mm; Øa=162mm, h=36mm; top plate Ø=176mm h=30mm) A roll of Teflon foil (0.5 mm thick; Øi=98mm; Øa=206mm; h=230mm) was measured for general interest. This roll was also investigated by the emanation method at Heidelberg [12] for ^{226}Ra surface contamination, respectively the ^{226}Ra supported emanation of the bulk material [22].

As mentioned in the introduction we used the most prominent lines of the daughter nuclides ^{214}Pb, ^{214}Bi and ^{212}Pb, ^{208}Tl to determine the concentrations of ^{226}Ra and ^{228}Th, since in all samples Rn emanation can be neglected. Also for Teflon this is ruled out by the measured emanation rate of ≤ 0.26 mBq/kg ^{222}Rn for the complete roll [22], which scales to about ≤ 23 μBq/kg[11] by taking into account the ^{222}Rn diffusion properties for Teflon. The efficiencies have been estimated from Monte Carlo simulations [1] based on the code GEANT 3.21 (CERN Program Library). Uncertainties of the simulations have been tested with calibration muckups to be below 5 %. Concentrations of ^{210}Pb in lead have been evaluated via the 803.1 keV line of ^{210}Po. The high radio-purity level found in Pb and Cu makes both shielding material well suited for rare event experiments, but especially for GERDA [4]. It is assumed that the low concentration of ^{226}Ra and ^{228}Th is generally valid for good lead

[10] variations in ^{222}Rn concentrations between about 200 μBq/m^3 and 3 mBq/m^3 have been measured in standard bottled nitrogen with clear indication of ^{226}Ra contamination in the cylinder from which the high activity has been extracted [18]

[11] Zuzel G., private communication, calculation based on measurements of the diffusion coefficient and of the solubility by Mueller W. Master thesis, University of Heidelberg (1978)

qualities and after further verification may be also for electrolytic Cu. The higher ^{207}Bi and ^{60}Co concentrations in the Pb of DowRun quality might be due to a contamination introduced at the company during the cutting of the recess in the plates to fit around the detector. For the Boliden lead quality the cutting was done at the workshop at MPI with the usual care to avoid cross contamination.

Table II: Measured radionuclide concentrations in typical shielding materials and in Teflon®. Uncertainties with coverage factor k = 2; upper limits are decision thresholds, both according to [23]. The time denotes the live time of the measurement.

material	weight	time	specific activity [μBq/kg]			
	[kg]	[d]	^{226}Ra (U)	^{228}Th (Th)	^{40}K	various
lead (DowRun)	144.6	101.7	< 29	< 22	440 ± 140	98 ± 24 ^{207}Bi; 180 ± 20 ^{60}Co, (2.7 ± 0.4)x10^{7} ^{210}Pb
lead (Boliden)	144.3	75.0	< 46	< 31	460 ± 170	< 13 ^{207}Bi; < 11 ^{60}Co; (2.3 ± 0.4)x10^{7} ^{210}Pb
lead (Roman[12])	22.1	37.2	< 45	< 72	< 270	< 19 ^{207}Bi; < 25 ^{60}Co; < 1.3 10^{6} ^{210}Pb
copper (LENS)	125.0	100.7	< 16	< 19	< 88	< 10 ^{60}Co
stainless steel foil	38.1	80.1	600 ± 200	200 ± 100	1800 ± 600	18000 ± 1000 ^{60}Co
old ships iron	47.29	42.4	150 ± 40	460 ± 140	1000 ± 400	230 ± 40 ^{54}Mn; < 18 ^{60}Co; < 30 ^{137}Cs; < 20 ^{58}Co
Teflon	12.35	20.9	< 160	< 160	1500 ± 240	< 70 ^{137}Cs

It is astonishing that ^{40}K is lower in the ancient roman lead than in modern lead. Also for the LC2 lead (about 0.4 mBq/kg ^{210}Pb) used in the HDM experiment a ^{40}K concentration of about (0.31 ± 0.3) mBq/kg was found by neutron activation [24].
The stainless steel has unusual low concentrations of ^{226}Ra and ^{228}Th (see e.g. [3]) but rather high ^{60}Co content. The old ships iron is even lower in ^{226}Ra, and only slightly higher in ^{228}Th. However the contribution of this material from which the screws of GeMPI (see section 2.2) have been fabricated to the background of GeMPI is not negligible. The decision for the use of this material was based on a measurement with a less sensitive Ge-spectrometer at Heidelberg, which resulted only in upper limits at the mBq/kg level.
Teflon® proved to be rather free of ^{226}Ra and ^{228}Th impurity, but ^{40}K is unusually high compared to a measurement on the same batch of Teflon material with neutron activation analysis[13]. The preliminary result of 0.7mBq ^{40}K/kg (22 ppb K) is in the same ballpark as that of other NAA of K in Teflon[14]. Also earlier Ge-measurements of smaller more bulky samples of Teflon by the authors did not show indications of ^{40}K contamination above the sensitivity level of a few mBq/kg. An explanation could be that a K-rich substance was placed on the surface during the foil forming process, which was removed in the sample preparation (acid cleaning etc.) procedure for NAA. Further investigations are planned to solve the contradiction between the γ-ray and the neutron activation analysis. Apart from the suspected local surface contamination of ^{60}Co and ^{207}Bi on the DowRun lead and of the ^{40}K on the Teflon foil there is no indication of surface contamination for the other investigated samples, even though only wipe cleaning with alcohol soaked paper was applied in case of the lead and copper sample preparation after machining. Their surface area corresponds to about 1.6 m^2 and 1.1 m^2. The steel roll and the Teflon® roll were measured as delivered except for outer surface wipe cleaning. Rust from the old ships iron plates (about 45 mm thick) was removed with diluted nitric acid.

[12] a sample of this lead (see also [20]) has been measured for the experiment CUORE [21]
[13] Cattadori C., private communication;
[14] Piepke A., private communication

3.4 Cosmogenic production rates in copper

One set of the two identical produced Cu plate samples was exposed for 270 days at a hall of LNGS (altitude 1038 m a.s.l., latitude 42° 27' N) under an averaged roof thickness of about 20 g/cm^2. The 33 mm thick slabs were placed side by side as a single layer on a pallet during the exposure.
The average total count rate (100 – 2730 keV) of the activated sample at end of counting (106.2 days after the end of the exposure) was 447.3 d^{-1}, compared to the 41.2 d^{-1} of the normal background listed in Tab. I.
Table IV lists the evaluated specific activity for 9 radionuclides from the spectrum measured over 103 days that has been scaled to saturation. The saturation activity corresponds to the cosmogenic production rates. Also the following upper limits for the primordials were obtained for this set of copper plates: < 35 µBq/kg ^{226}Ra; < 20 µBq/kg ^{228}Th; < 110 µBq/kg ^{40}K. They are well in agreement with the result of the unexposed set (Table II).

Table III Cosmogenic production rates (saturation activity) in Cu, Uncertainties according to [23] with coverage factor k = 1.

radionuclide	**half-life**	**saturation activity [µBq/kg]**
^{56}Co	77.31 d	230 ± 30
^{57}Co	271.83 d	1800 ± 400
^{58}Co	70.86 d	1650 ± 90
^{60}Co	5.27 y	2100 ± 190
^{54}Mn	312.15 d	215 ± 21
^{59}Fe	44.5 d	455 ± 120
^{46}Sc	83.79 y	53 ± 18
^{48}V	15.97 d	110 ± 40

The cosmogenic radionuclides are typical products of spallation reactions, since at least 4 nucleons and up to 18 nucleons have to be emitted after the neutron or the proton interacted with ^{63}Cu. ^{60}Co reaches with a production rate of 2.1 mBq/kg the highest saturation activity and thus strongly exceeds the activity of any other radio-impurity listed in Table II for Cu. This demonstrates the importance of limiting the cosmic ray exposure if Cu is used as construction material for rare event experiments. Cosmogenic production rates deduced from a reconstruction of not well documented sea level exposure of Cu used for the HDM experiment [8] yielded similar results: 1 mBq/kg ^{60}Co; 1.7 mBq/kg ^{58}Co; 1 mBq/kg ^{57}Co and 0.35 mBq/kg ^{54}Mn. The ^{60}Co activity in the unexposed set of Cu plates was undetectable at a limit of 10 µBq/kg (Table II) and thus indicates a sea level exposure of less than about 14 days. In Fe the production rate for ^{54}Mn is even higher than in Cu [8], therefore it was still detectable in the old ships iron (Table II), although this sample was resting for many ^{54}Mn half lives at a shielded position in the floor of the Heidelberg low-level laboratory. No activation was detectable in the lead samples, which however have not been exposed by purpose for a longer period. There were also no indications by earlier investigations of the authors, however performed at a lower sensitivity level.
The measured production rates are useful to study and test model calculations for cosmogenic production, an issue of growing importance for upcoming rare event experiments.

4 Future developments

The high statistics spectrum of the HDM ßß experiment has been modelled by Monte Carlo simulations in order to localize the residual contamination in the cryostat systems of the individual detectors [14, 17]. This method is exploiting the different degrees of attenuation for γ-ray emissions of different energies from different materials and different locations in the experimental set up. The result of this analysis and earlier ones [15, 25] is that the most probable location of the primordial activities is the copper of the detector cryostats. In Table V the thus deduced concentrations are compared to the measured ones of the same NOSV copper quality with GeMPI. The most plausible explanation of the large spread in primordial concentrations among the HDM cryostats and their much higher contamination (one exception – ^{228}Th in ANG 2) with respect to the measured bulk material is that the activity is surface correlated. The model for the simulation was based on the assumption that the activity is homogeneously distributed. A variation in surface cleanliness is also plausible from the fact that different people have assembled the HDM detectors over a period of 4 years under not always identical conditions.

Table IV Contamination in Cu according to Monte Carlo calculation for the HDM detectors [17] and measured with GeMPI.

location of copper	**activity [μBq/kg]**		
Cu of cryostat Nr.	^{226}Ra	^{228}Th	^{40}K
ANG 1	168 ± 8	84 ± 7	236 ± 61
ANG 2	91 ± 4	10 ± 3	78 ± 22
ANG 3	105 ± 5	84 ± 5	927 ± 46
ANG 4	115 ± 3	87 ± 4	199 ± 4
ANG 5	100 ± 4	26 ± 4	1632 ± 49
Cu measured with GeMPI	≤ 16	≤ 19	≤ 88

A clear indication follows also from count rate variations by about a factor 30 of the ^{210}Po α-peak observed in the high energy spectra of the 5 detectors [15]. The location of this contamination must be the area around the core or in it, since only there alphas are not shielded by inactive layers of the Ge crystal.
From these findings it is obvious that a strong reduction of surface and mass of the several layers of cladding material around the crystal (see FIG. 1) may open the possibility for further background reduction. This idea [6] is now being realized in the GERDA experiment [4], a further development of a former proposal [26, 27].
The basic design is to contact and hold the Ge-crystals with a minimum of highly radio-pure material, to deploy them in liquid nitrogen or liquid argon for cooling and to shield them against external radiation in a deep underground location. It has been demonstrated that liquid nitrogen can be made highly radio-pure [28, 29]. The high insulation property of the liquid gases allows installing a larger array of Ge-diodes in a compact way with only little distance to each other. GERDA aims to reduce the background in the energy region around the $Q_{ßß}$-value of ^{76}Ge at 2.039 MeV by two to three orders of magnitude compared to what has been reached in HDM [16]. It is hoped that the same reduction factor can be obtained also for the whole energy range from 50 – 2800 keV. A further prerequisite is that cosmogenic activation of the crystals from sea level exposure needs more control than achieved so far.

If once cryogenic liquid type Ge-spectroscopy is established, a further step in screening sensitivity would be reachable, may be even down to the nBq/kg range. Limitations will arise from the increasing measuring periods needed to arrive at useful counting statistics from such low activity concentrations, if not compensated by larger sample masses and multi-Ge detector arrays. Therefore, an application in life sciences seems to be rather limited, except may be for some very special key measurements. For example cosmogenic activation of materials exposed at surface or shallow depth could be used as tracer for their residence time. Copper samples of about 100 g could be sufficient to measure cosmogenic radio-nuclides with different half-lives (see Table IV). Gamma-active radioisotopes produced by accidental neutron exposures could be an issue in radiation protection.

5 Conclusions

It could be demonstrated that underground low-level germanium spectrometry can reach a sensitivity level in the range of 10 μBq/kg, corresponding to about 10^{-12} g/g ^{238}U/^{232}Th and about 10^{-9} g/g K. This has been achieved by a combination of background reduction, mainly as a result of extensive material screening of the construction materials and a favourable large sample capacity. Some key measurements of materials frequently used in rare event projects as copper and lead are helpful for the design of upcoming second generation experiments. To overcome the relative slow sample throughput due to the long counting time there are two additional GeMPI type Ge spectrometers under construction, of which one is already in the testing phase at LNGS [30].

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