DETERMINATION OF RADIOACTIVE TRACE ELEMENTS IN ULTRA LOW BACKGROUND DETECTORS BY MEANS OF NEUTRON ACTIVATION ANALYSIS

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In this paper new analytical methods for the determination of naturally occurring radionuclides are being presented. They combine neutron activation, radiochemical separation and coincidence counting techniques. For complex matrices such as organic liquids and silicon we have obtained detection limits lower than 10^{-14}g/g for Th, U, La and lower than 10^{-12}g/g for Cd, In, K, Lu, and Rb with radiochemical separation methods geared to the nuclides investigated. The β-γ coincidence counting techniques used for the determination of U, Th and Lu in the ultra trace region are discussed in detail, with recorded spectra and applied selection criteria for the evaluation of decay events. Impacts of the results on low level experiments in the field of astro and particle physics are being discussed as well as the advantage of neutron activation analysis which is sensitive to most naturally occurring radionuclides.

1 Introduction

Research towards a new generation of detectors in the field of weakly interacting particles dark matter search and double beta decay has brought up the need to set foot on new paths for low background detectors. These detectors are designed to measure rare interactions of particles at the lowest possible background being shielded from cosmic and natural radioactivity since this activity can mimic the type of interaction one is interested in [1].

Closely connected to this is the question of radioactive contaminants introduced to the detectors by the shielding, electronic components and detector components themselves, thus limiting the sensitivity by their intrinsic activity. This has initiated some efforts in the field of analytical chemistry and particle physics in order to develop new analytical methods to approach the question of background reduction from another side.

Besides cosmogenic and anthropogenic radioactivity, a class of primordial elements which are ubiquitous due to their natural occurrence can be a source of background in low level detectors by their decay and the decay of their progenies. The most relevant quasistable isotopes are listed in Table 1.

In the case determination of the unstable isotope itself is not viable by γ-spectroscopy, β-spectroscopy or α- spectroscopy there is an alternative way to determine the concentration of unstable, naturally occuring isotopes by applying sensitive methods of trace analysis.

Comparing different analytical methods neutron activation analysis (NAA) turns out to be a method sensitive enough to determine some isotopes in the ultra-trace region, while merging advantages of large sample quantities with reliable detection techniques.

Table 1. Naturally occurring radioactive isotopes with their half-lives, relative abundances and decay modes [10]. The specific activity is given in Bq g^{-1} of element assuming natural isotopic composition.

Isotope	$T_{1/2}$ [a]	Rel. Abundance [%]	Decay mode	Specific activity $[g^{-1}s^{-1}]$
^{113}Cd	$9\cdot10^{15}$	12.22	β^-	$1.6\cdot10^{-3}$
^{152}Gd	$1.1\cdot10^{14}$	0.20	α	$1.6\cdot10^{-3}$
^{174}Hf	$2.0\cdot10^{15}$	0.162	α	$6.2\cdot10^{-5}$
^{115}In	$4.4\cdot10^{14}$	95.7	β^-	$2.5\cdot10^{-1}$
^{40}K	$1.28\cdot10^{9}$	0.0117	$\varepsilon\ \beta^-\ \beta^+\ \gamma$	$3.0\cdot10^{1}$
^{138}La	$1.05\cdot10^{11}$	0.0902	$\varepsilon\ \beta^-\ \gamma$	$8.2\cdot10^{-1}$
^{176}Lu	$3.8\cdot10^{10}$	2.59	$\beta^-\ \gamma$	$5.1\cdot10^{1}$
^{144}Nd	$2.29\cdot10^{15}$	23.80	α	$9.6\cdot10^{-3}$
^{186}Os	$2.0\cdot10^{15}$	1.58	α	$5.6\cdot10^{-4}$
^{190}Pt	$6.5\cdot10^{11}$	0.01	α	$1.1\cdot10^{-2}$
^{87}Rb	$4.8\cdot10^{10}$	27.835	β^-	$8.8\cdot10^{2}$
^{187}Re	$5\cdot10^{10}$	62.60	β^-	$8.9\cdot10^{2}$
^{147}Sm	$1.06\cdot10^{11}$	15.0	α	$1.3\cdot10^{2}$
^{148}Sm	$7\cdot10^{15}$	11.3	α	$1.4\cdot10^{-3}$
^{180}Ta	$>10^{15}$	0.012	$\varepsilon\ \beta^-\ \gamma$	$<8.8\cdot10^{-6}$
^{123}Te	$1.24\cdot10^{13}$	0.908	ε	$7.9\cdot10^{-2}$
^{232}Th	$1.405\cdot10^{10}$	100	α sf	$4.1\cdot10^{3}$
^{238}U	$4.468\cdot10^{9}$	99.2745	α sf	$1.2\cdot10^{4}$
^{50}V	$1.4\cdot10^{17}$	0.250	$\varepsilon\ \beta^-\ \gamma$	$4.7\cdot10^{-6}$

In addition NAA has the advantage of less blank problems than other analytical techniques and is also capable of analyzing matrices which are difficult to decompose.

2 Neutron Activation Analysis (NAA)

Basic Principles

As the sensitivity of analytical techniques is often limited by matrix effects it is important to have a look at the matrix. The most common reaction for the determination of trace elements by NAA is $^{A}Z + n \Rightarrow {}^{A+1}Z + \gamma$ where the γ is emitted with an energy characteristic of the nucleus ^{A+1}Z decaying with a half life $T_{1/2}$. This γ is detected in a NaI or Ge-spectrometer which allows the determination of the concentration of nuclei ^{A}Z in a matrix by the activity of the nuclei ^{A+1}Z. The activity of activated nuclei is given by the parameters, i.e., neutron capture cross section, neutron flux, exposure time and decay time. As not only the nuclei of the trace element Z but also the matrix is exposed to the neutrons the activity produced by the matrix has to be equal or less than the activity of ^{A+1}Z during the time of the measurement in the relevant energy range.

This usually restricts the application of NAA to matrices which have much lower neutron capture cross sections and/or much shorter half lives than the isotopes to be detected. These demands are satisfied by light elements (e.g. H, C, N, O, F and Si) which are often constituents of matrices. This demand can be avoided by a chemical separation of the matrix and trace elements or by the use of long cooling times if the matrix activity decays faster than the activity of the trace element.

This makes the NAA an ideal tool for the detection of trace constituents in H_2O, Si, organic matrices and plastics which are used for the construction of low level detectors.

Increasing the sensitivity of NAA

The sensitivity of NAA is not only limited by the matrix as mentioned above but it is also determined by the activation parameters illustrated in Fig. 1. Starting from sample preparation in clean boxes or clean rooms the samples to be analysed have to be handled in PFA (perfluoroalkoxy) and quartz vessels before and in synthetic quartz vessels during irradiation to reduce the blank value of the analysis [1]. The irradiation parameters of sample mass and neutron flux should be as large as possible while the irradiation time can be adapted to the matrix and to the trace elements to be determined.

In order to obtain a high detection power it is necessary to keep the activity in the counting system from the irradiated sample or from the counting system itself as low as possible.

A radiochemical separation of activated nuclei from the matrix can improve the sensitivity significantly because of several reasons. In the ideal case the induced activity can be split up into two or more groups containing the matrix activity, the activity of other interfering traces and the activity of the radionuclide of interest. This minimises the activity and thereby the background in the counting chamber of the spectrometer.

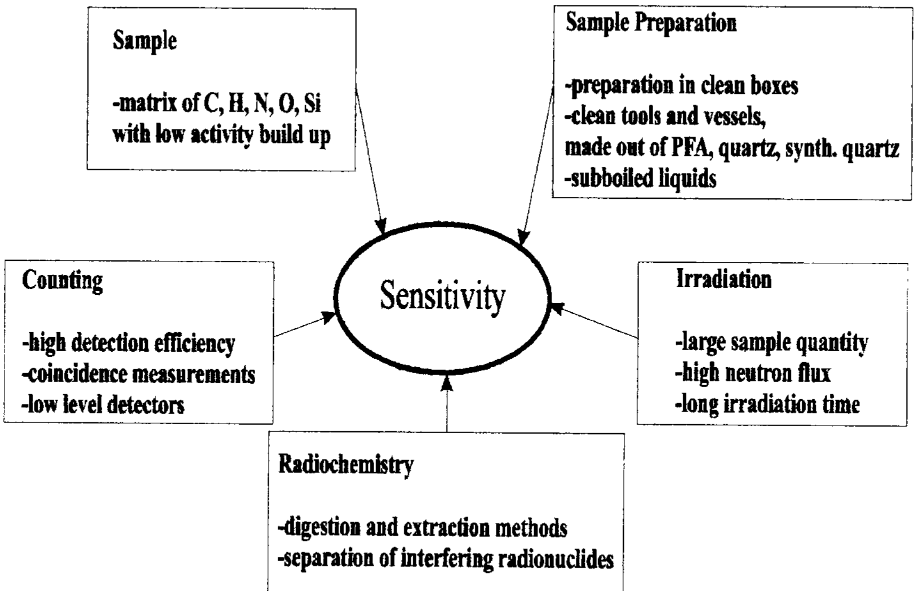

Fig. 1. Factors fixing the sensitivity of neutron activation analysis

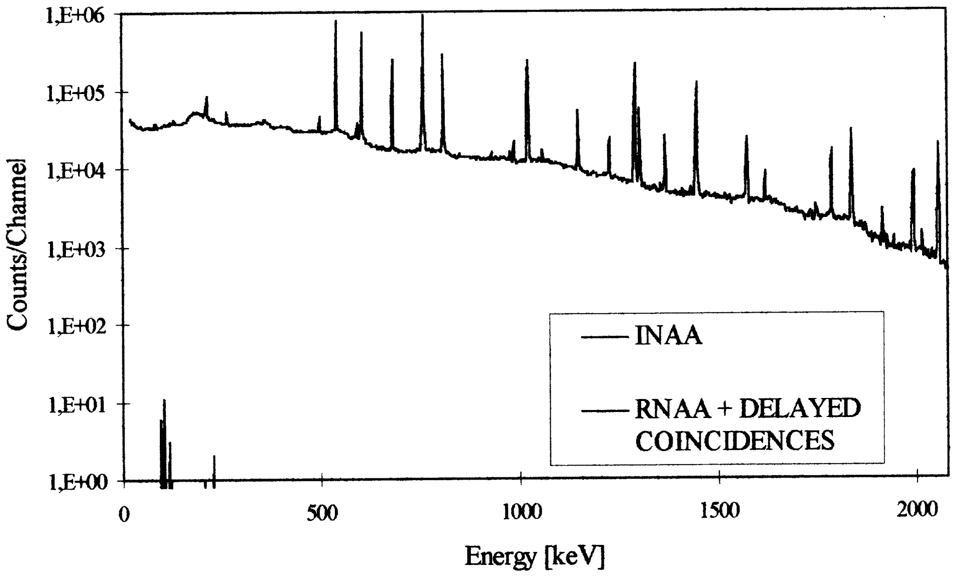

Fig. 2. The γ spectrum of an irradiated liquid scintillator prior to and after a radiochemical separation combined with coincidence counting techniques. The coincidence counting mode was geared to the detection of ^{239} Np which is the indicator radio nuclide for ^{238}U

Another important factor which governs the sensitivity is the detection efficiency of the emitted γ-rays. As a gain of detection efficiency usually not only increases the number of decays of traces which are to be determined but also the number of background events, the signal/noise ratio can not be improved above a certain limit by the increase of efficiency due to physical and financial restrictions. A further improvement in the signal/noise ratio can be achieved if coincidence or anticoincidence counting modes are used. This can be realised by γ-γ-(anti)coincidence or β-γ-(anti) coincidence counting modes to enumerate the most common ones. For some isotopes even delayed β-γ-e^--coincidence may apply if the indicator radionuclide populates an isomeric state providing an additional signature of the decay [2,3].

An optimisation of these factors can improve the sensitivity by some orders of magnitude as is illustrated in Fig. 2 [4].

3 Experimental

Experimental set up for β-γ coincidences

For many applications liquid scintillators are a good choice providing high efficiency, good timing resolution and sufficient energy resolution for the detection of α-particles, β-particles and conversion electrons. Combined with a Ge- spectrometer some of the counting modes mentioned above can be realised. In order to measure the emitted particles as well as the photons the radiochemically processed sample is dissolved in a liquid scintillator which is viewed from one side by a photomultiplier and from the other side by a Ge-detector. Both detectors can provide timing and energy information which allows building triggers geared to the decay of the indicator radionuclide. The set-up we have used in connection with different types of Ge-detectors is shown in Fig. 3.

Information from two detectors are recorded by a Camac data acquisition system which measures the energy deposed in the scintillator and the Ge-detector as well as providing timing information for these events. The recorded data can be evaluated off line. The events are selected by their γ-energy, the β-energy, the conversion electron energy and the time difference between β-decay and conversion electron emission as is shown for a spectrum of a ^{239}Np calibration activity in Fig. 5.

Besides the delayed β-γ-conversion electron coincidence used for the determination of U described in the next chapter, we have applied the β-γ coincidence counting mode in order to determinate Th and Lu. Although the β-γ coincidence does not reduce the intrinsic background due to the similar β endpoint of the Th and Lu compared to the interfering nuclides, the external background originating from activity in the counting chamber can be suppressed. This β-γ coincidence can be applied effectively if the intrinsic activity is low and the sample has to be counted for several weeks, a period during which the external background would worsen the detection limit for indicator radionuclides with half lives of weeks or months.

An effective background suppression can be achieved instead by a β-γ coincidence if the β-endpoint of the indicator radionuclide differs significantly from the β-endpoint of the interfering nuclides. This allows to set a cut on the β- endpoint to suppress the interfering activity. β-γ Anticoincidences can be used as well to search for radionuclides decaying by electron capture such as ^{51}Cr, ^{64}Cu, ^{65}Zn, ^{75}Se, ^{85}Sr or ^{97}Rb to supress interfering activity if this activity is associated with β – γ emission.

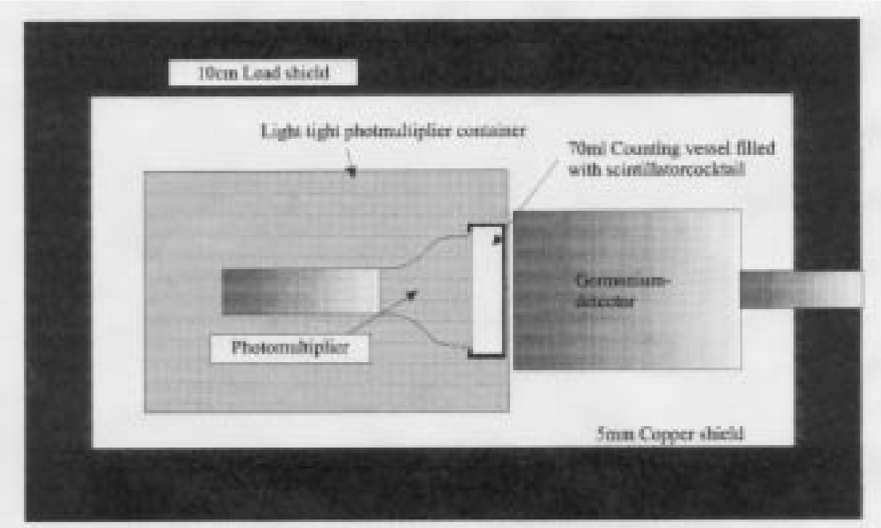

Fig. 3. Experimental set-up used for the measurement of a sample dissolved in a liquid scintillator.

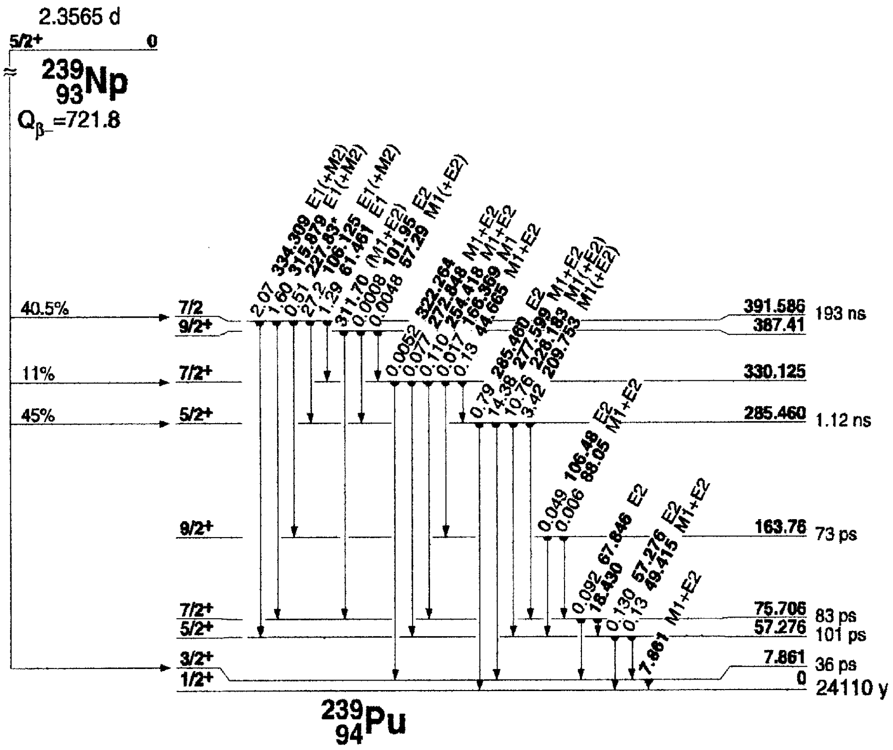

Fig. 4. Decay scheme of ^{239}Np showing the isomeric state with a half life of 193ns. Taken from reference [10]

Spectra and cuts: An example

Taking a closer look at the decay scheme of ^{239}Np (Fig. 4) which is the indicator radio-nuclide for ^{238}U we can see that the β^- decay of ^{239}Np populates an isomeric state of ^{239}Pu with a probability of 40.5% which is depopulated by the emission of γs and conversion electrons. This implies that the number of emitted conversion electrons decays exponentially with the half life of the isomeric state. It offers the possibility not only to use the information on the energy of emitted βs, γs, and conversion electrons but also of the time delay between βs and conversion electrons as a signature in order to discriminate interfering activity.

Since the intrinsic sample activity is often caused by pure β emitters it is suppressed effectively by the application of cuts on the β endpoint, the conversion electron energy and the delay time between emitted β and conversion electrons. The efficiency of the applied cuts can be determined by applying the same cuts to a known activity of ^{239}Np. Finally the activity of ^{239}Np can be deduced from the γ spectrum by summing up the number of events in the 103.7keV, 99.5keV, and 106.1keV peaks.

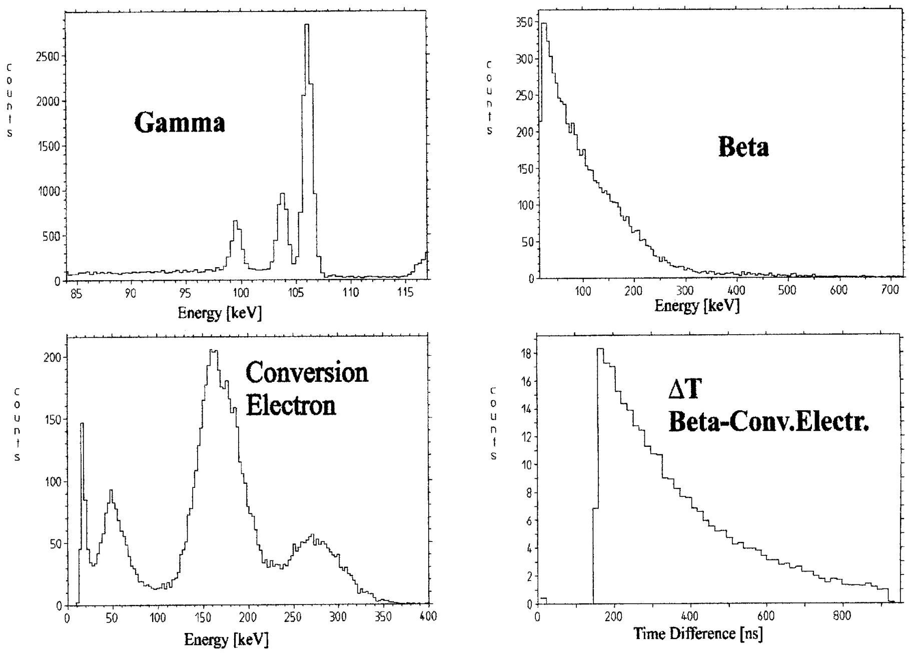

Fig. 5. Spectra recorded with the experimental set up. Clockwise the spectra of γ-energy, β-energy, conversion electron energy and time difference β-conversion electron are shown

4 Results

Trace elements in water

The contents of trace element in high purity water are of interest for several reasons. It is not only one of the most common fluids used in analytical laboratories but it also has cleaning capacities as an extraction medium with the capability to take up ionic impurities of liquid-liquid extractions. For low level experiments ultrapure H_2O fulfils several demands. It can not only serve as a cleaning fluid but it can also be used as a shield against γ rays since it is very low in radiocontaminants itself.

The irradiation of high purity water and organic solvents has been carried out at the research reactor FRMI in Garching, Germany. An irradiation facility has been developed here which allows the irradiation of liquid samples subjected to radiolysis for up to several days. In order to prevent a pressure build up the gas produced during irradiation is released into the pool water. Typically 250 mL samples were irradiated for up to 100 h at a thermal neutron flux of $7 \cdot 10^{12}\ s^{-1}cm^{-2}$.

The analysis of water is relatively simple as the water can be evaporated after irradiation and the evaporation residue can be processed radiochemically usually without any pre-treatment. This radiochemical treatment consists of separating the evaporation residue into two groups [7]. One group contains the indicator radionuclides with half lives in the day range and is counted directly, the other group contains

Np (U), Pa (Th) and Lu, and is dissolved in a liquid scintillator cocktail and counted in the β-γ-conversion electron and the β-γ coincidence mode described above. The results obtained for water which was distilled twice in a quartz subboiling still are compiled in Table 2.

Trace elements in organic scintillators

A new group of large scale particle detectors uses organic scintillators for the detection of neutrinos. The high light yield of the organic solvents offers low energy thresholds and good energy resolution associated with short signal rise times and α-β particle discrimination capabilities. They are also an attractive choice for active vetoes of low level experiments where the scintillator serves both as a particle detector and as a shield.

The low solubility of ionic impurities together with distillations in the manufacture assure a high initial purity of the solvents that the scintillators are based upon.

We have investigated two scintillators which were tested in the Borexino prototype, an experiment which is dedicated to the measurement of solar neutrinos in the low energy range. The first one is a scintillator consisting of 1,2,4- trimethylbenzene (PC) and 2,5-diphenyloxazole (PPO). The latter is dissolved as a primary wavelength shifter at a concentration of 1.5g L^{-1} in the solvent. The second one is composed of phenyl-o-xylylethene (PXE) and p-diphenylbenzene (PT) which is added as a primary wavelength shifter at a concentration of 3 g L^{-1} to the solvent.

Although organic solvents are severely degraded and decomposed by the neutron irradiation they can be irradiated up to 100 hours in the irradiation facility with appropriate gas release [6]. The radiochemical processing following the irradiation after a cooling time of two or three days is more complicated than the processing of aqueous samples. The irradiated solvents are subjected to acidic extraction transferring the activated trace elements into an acid. This acid is evaporated and split up into two groups by liquid-liquid extraction or ion exchange containing activities which can be measured by the counting modes mentioned above [5]. The compilation of trace elements given in Tables 3 and 4 and shows that organic scintillators can be produced with exceptional purity fulfilling the even the demands for experiments like Borexino which imposes stringent demands on the content of radioactive contaminants.

Table 2. Trace element concentrations in subboiled, high purity water. The limits are given for the 90% confidence level [9].

Element	Concentration [g/g]	Element	Concentration [g/g]
Au	$<5\cdot10^{-15}$	Lu	$<7\cdot10^{-14}$
Cd	$<4\cdot10^{-13}$	Na	$<1\cdot10^{-13}$
Co	$3\cdot10^{-13}$	Rb	$<9\cdot10^{-13}$
Cr	$<4\cdot10^{-12}$	Sb	$<7\cdot10^{-14}$
Fe	$<3\cdot10^{-11}$	Sc	$<6\cdot10^{-14}$
In	$<5\cdot10^{-13}$	Th	$2\cdot10^{-15}$
Ir	$<5\cdot10^{-15}$	U	$4\cdot10^{-15}$
K	$<8\cdot10^{-13}$	W	$<2\cdot10^{-14}$
La	$<4\cdot10^{-15}$	Zn	$<2\cdot10^{-12}$

Table 3. PC/PPO based scintillator (see text). The limits are given for the 90% confidence level

Element	Concentration [g/g]	Element	Concentration [g/g]
Ag	$4\cdot10^{-12}$	Lu	$<8\cdot10^{-16}$
Au	$2\cdot10^{-14}$	Mo	$<5\cdot10^{-13}$
Cd	$<1\cdot10^{-12}$	Na	$<2\cdot10^{-12}$
Ce	$<2\cdot10^{-13}$	Rb	$<7\cdot10^{-13}$
Co	$3\cdot10^{-14}$	Sb	$3\cdot10^{-14}$
Cr	$7\cdot10^{-13}$	Sc	$<3\cdot10^{-15}$
Cs	$<1\cdot10^{-13}$	Sm	$<2\cdot10^{-15}$
Fe	$<2\cdot10^{-11}$	Th	$<2\cdot10^{-15}$
In	$<2\cdot10^{-12}$	U	$<2\cdot10^{-16}$
Ir	$<2\cdot10^{-14}$	W	$<3\cdot10^{-14}$
K	$<4\cdot10^{-12}$	Zn	$<4\cdot10^{-12}$
La	$2\cdot10^{-14}$		

Table 4. PXE/pTP based scintillator (see text). The limits are given for the 90% confidence level.

Element	Concentration [g/g]	Element	Concentration [g/g]
Ag	$<2\cdot10^{-12}$	Lu	$<7\cdot10^{-16}$
Au	$<2\cdot10^{-15}$	Mo	$<7\cdot10^{-13}$
Cd	$<2\cdot10^{-12}$	Na	$6\cdot10^{-11}$
Ce	$<2\cdot10^{-12}$	Rb	$<8\cdot10^{-12}$
Co	$<6\cdot10^{-13}$	Sb	$3\cdot10^{-13}$
Cr	$3\cdot10^{-11}$	Sc	$<2\cdot10^{-14}$
Cs	$<8\cdot10^{-12}$	Sm	$4\cdot10^{-15}$
Fe	$<2\cdot10^{-10}$	Th	$<3\cdot10^{-15}$
In	$5\cdot10^{-12}$	U	$<6\cdot10^{-16}$
Ir	$<2\cdot10^{-14}$	W	$1\cdot10^{-13}$
K	$<8\cdot10^{-12}$	Zn	$7\cdot10^{-11}$
La	$2\cdot10^{-14}$		

5 Outlook

The question now arising is: which is the ultimate level of activity that can be achieved with a liquid scintillation detector? This intrinsic activity sets a limit to the activity which can be measured in low level detectors if background radioactivity originating from other sources and cosmogenic activity can be suppressed adequately. In the case of Borexino ten neutrino events per day have to be detected in a target of 100 t of liquid scintillator with a level of background activity comparable to the signal [7].

In Table 5 the specific activity is compiled for the detection limits obtained, showing that the analytical procedure presented is capable to set limits on the detector

Table 5. Activity for determined concentrations of trace elements in a liquid scintillator. For the ^{238}U and ^{232}Th chain only the activity of ^{238}U and ^{232}Th is taken into consideration.

Element	Decays [kg^{-1}a^{-1}]	Element	Decays [kg^{-1}a^{-1}]
^{113}Cd	$<5.0\cdot10^{-5}$	87Rb	<20
^{115}In	$<1.6\cdot10^{-2}$	147Sm	$<8.2\cdot10^{-3}$
^{40}K	<3.9	^{232}Th	$<2.6\cdot10^{-1}$
^{138}La	$5.2\cdot10^{-4}$	238U	$<7.6\cdot10^{-2}$
^{176}Lu	$<1.3\cdot10^{-3}$	All	<24

impurities which corresponds to a few decays per (kg.year). This sensitivity can not only be used for quality assurance of the utilised materials but also for the development of cleaning and refining procedures.

With cuts on the energy threshold, particle discrimiation capabilities and other signatures as time correlations one can achieve even lower levels of background for this type of detector which are not taken into consideration for the given estimations.

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