Ultra sensitive Determination of K, Th, U and other Trace Impurities in Liquid Organic Scintillators with NAA

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Abstract

In this paper we present an analysis NAA technique to determine ultratraces of K, Th, U and other trace impurities in liquid organic scintillators, which are discussed as ultrapure detector materials for low background experiments. A combined optimization of relevant factors for sensitive NAA has been realized, leading to a sensitivity for U down to 10^{-16}g/g. Samples of 250 ml have been irradiated up to 120 h at a thermal neutron flux of $5 - 8 \cdot 10^{12}\mathrm{cm}^{-2}\mathrm{s}^{-1}$. Acidic extraction, wet ashing and TBP-extraction are used for radiochemical separations. Finally, sophisticated coincidence techniques are applied for a further increase of sensitivity.

Introduction Underground experiments as solar neutrino experiments, search of dark matter, study of double beta decays, and in general all detectors designed to identify rare events, need very low background. The background problems are particularly challenging when the detection threshold is within the energy range of natural radioactivity.

The solar neutrino experiment BOREXINO [1], for which this work is carried out, uses liquid organic scintillator as target and detector material. The maximum acceptable content for U and Th in this scintillator is in the range of 10^{-16}g/g, for K in the range of 10^{-14}g/g. But also other quasistable nuclides such as ^{176}Lu, ^{138}La, ^{115}In, ^{113}Cd or ^{87}Rb might be relevant background sources.

Analysis techniques are therefore needed to measure potential liquid organic scintillators with such a sensitivity. When using ICP-MS, which is common for the analysis of aqueous samples, a direct introduction of organic liquids is very difficult and previous decomposition will contaminate the sample very easily. For these reasons Neutron Activation Analysis methods have been developed at the Technical University in Munich to analyse liquid organic scintillators. To meet the high sensitivity requirements a combined optimization of several important factors for sensitive NAA has been carried out[3].

Experimental

Samples: So far the method was tested and applied to two scintillators so far. The first scintillator is composed of the solvent 1,2,4-Trimethylbenzene (PC) and the fluor 2,5-Diphenyloxazole (PPO), the second of the solvent Phenyl-o-Xylylethene (PXE) and the fluor p-Diphenylbenzene (TP). Both solvents originate from batches for the prototype detector CTF of the BOREXINO-detector, which were directly filled in thoroughly cleaned teflon and stainless steel containers at the refinery.

Sample preparation: The sample preparation before irradiation is carried out in a glove box supplied with filtered air, for which the cleanroom class has been determined to be below 10. The scintillator samples are poured without further treatment into 250 ml irradiation flasks out of synthetic quartz, which have been etched with conc. HNO_3/HF (1:1) and subsequently soaked in freshly subboiled HNO_3 (5%) and water for several days.

Irradiation: The samples are irradiated at the research reactor of the Technical University of Munich at Garching. The thermal neutron flux at the liquid irradiation facility is $5\text{-}8 \cdot 10^{12} \mathrm{cm}^{-2} \mathrm{s}^{-1}$. Because of contamination risks and focus on sensitivity the flux determination is carried out merely once or twice per reactor period with Zr- and Au-wires. The special design of the irradiation facility allows irradiation times up to 120 h. For a detailed description of this facility the reader should refer to the literature[6],[4]. *Radiochemial procedures:* After a cooling period of 2-3 days, the irradiated samples are prepared for counting. The high sensitivity requirements make it necessary to apply radiochemical procedures for separating interfering nuclides and for transfering interesting nuclides in scintillator cocktails for coincidence measurements with β's or conversion electrons. A scheme of the whole procedure is given in Fig. 1. Even without interfering nuclides radiochemical techniques would be necessary for the application of coincidence measurements. The irradiated scintillator can no longer serve as a scintillator, because the irradiation causes a severe degradation turning the samples into brown viscous liquids.

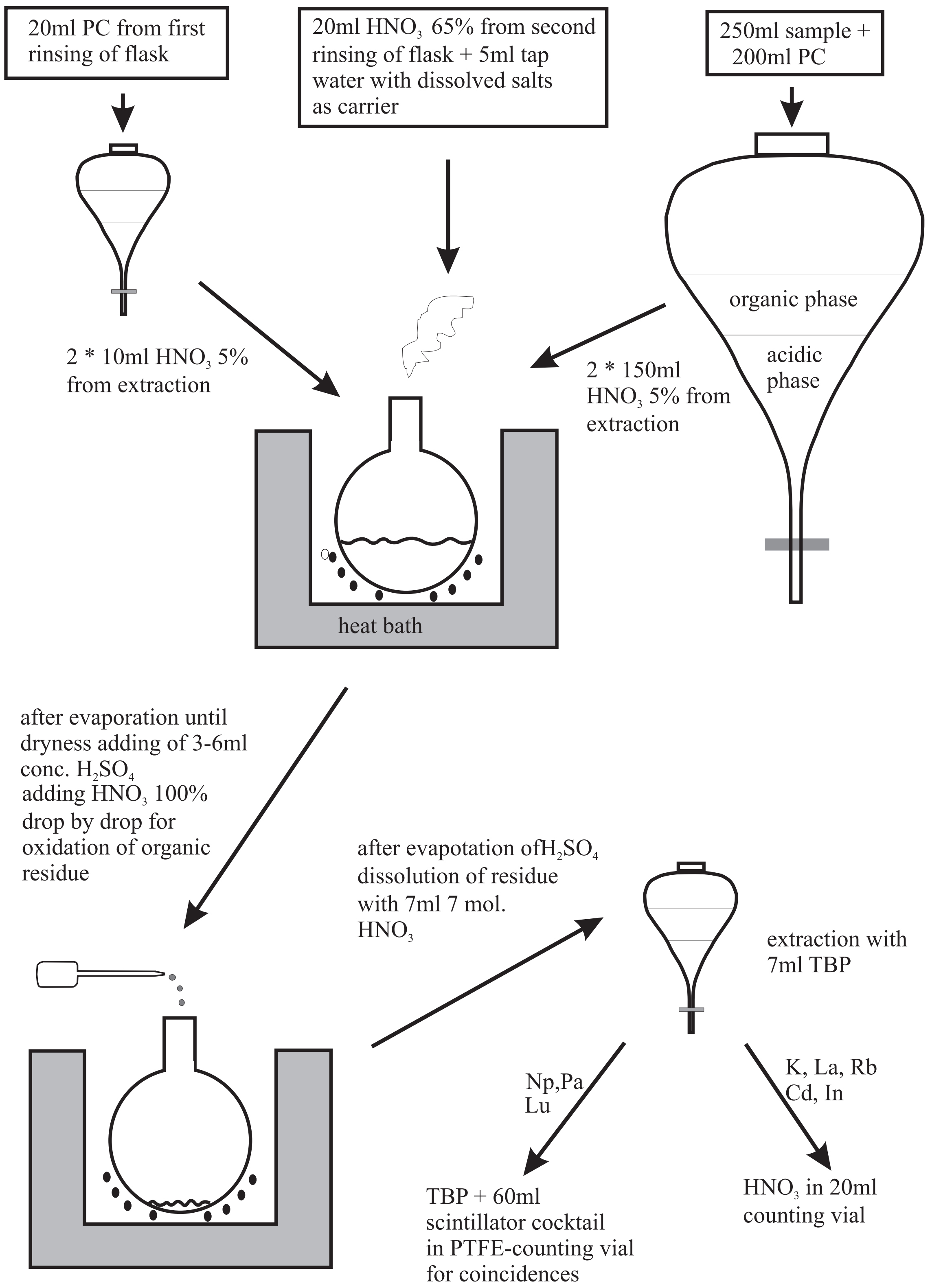

Figure 1: *The radiochemical procedure used for the irradiated scintillator samples. All tools in contact with the sample are made of PFA or quartz.*

While high temperature dry ashing and wet ashing of the whole sample proved to be unsuitable because of losses by volatization and safety problems, acidic extraction has been found to be a possible technique for separating interesting nuclides from irradiated scintillators.

For acidic extraction the samples are transferred from the irradiation flasks into a separatory funnel made of PFA. To reduce the viscosity of the samples 200 ml of PC are primarily added. Two extraction steps are carried out with 150 ml of HNO_3 (5%), each time shaking the funnel thoroughly for 15 mins. The phase separation takes about 30-60 min in both steps, which is much longer than acidic extractions of unirradiated organic liquid scintillators and can be only explained by the strong sample degradation. The acidic phases are drained in a 500 ml round flask made of quartz. To collect any remaining acid droplets, the organic phase is centrifuged after the second extraction step and the separated acid is also transferred into the round flask.

The drained irradiation flasks are rinsed twice with 10 ml PC to remove organic traces left behind. This PC is also subjected to acidic extraction and the acid is added to the 300 ml in the round flask. After drying the irradiation flasks with nitrogen they are finally rinsed twice with 10 ml hot 65After transferring the acid from rinsing into the round flask, the whole acidic phase is concentrated to 5 ml by putting the round flask into a heat bath. The usage of a surface evaporator turned out to be disadvantageous, because traces of organic liquid at the surface slow down the concentration process considerably.

Because this remaining organic residue would affect the optical properties of the scintillator cocktail, a low pressure wet ashing step is then carried out. Depending on the amount of organic material 3-6 ml of 98% H_2SO_4 are added to the concentrated acid and the liquid is heated above 200^0C. By adding 100 % HNO_3 drop by drop the organic residue completely decomposes. After a clear solution has been obtained the H_2SO_4 is evaporated until dry by increasing temperature and the remaining salt is dissolved with 5 ml 7 M HNO_3.

To separate ^{239}Np, ^{233}Pa and ^{177}Lu from many interfering nuclides such as ^{24}Na, a liquid-liquid extraction with 7 ml Tri-butyl-phosphate (TBP) is carried out in the final step shaking both phases in a 125 ml separatory funnel made of PFA for 5 min. Whereas the acidic phase is drained in a counting vial, the TBP is mixed with 60 ml commercial scintillator cocktail (Ultima Gold AB from Canberra Packard) and filled in a special counting vessel for coincidence measurements. This vessel is described in detail in a previous paper.

Radiotracers have not been added in the process for several reasons. For Np and Pa tracer solutions were not available. ^{237}Np can not be used, because it decays to ^{233}Pa, which is used as indicator radionuclide for Th. The quasistable isotopes ^{4}0K and ^{138}La could be used for ^{42}K and ^{140}La, but then nearly one gram of material is needed for the tracer in order to get a sufficient activity. Neutron-produced radiotracers could be only used for ^{177}Lu and ^{115}Cd, but there is a principle reason why the usage of tracers might only be restrictedly meaningful. Partition coefficients for radiotracers can be different than for the activated nuclei in the organic sample, which might exist in special chemical bindings after the activation process. The addition of carriers is also not possible for Np and Pa and therefore 5 ml tap water are added to the HNO_3 with the dissolved salts serving as a general carrier to saturate, for example, adsorption sites at the walls. To reduce adsorption losses all used containers are made of PFA or quartz and have been rinsed with tap water prior to use. A test of the radiochemical procedure has been carried out by tracer experiments described below.

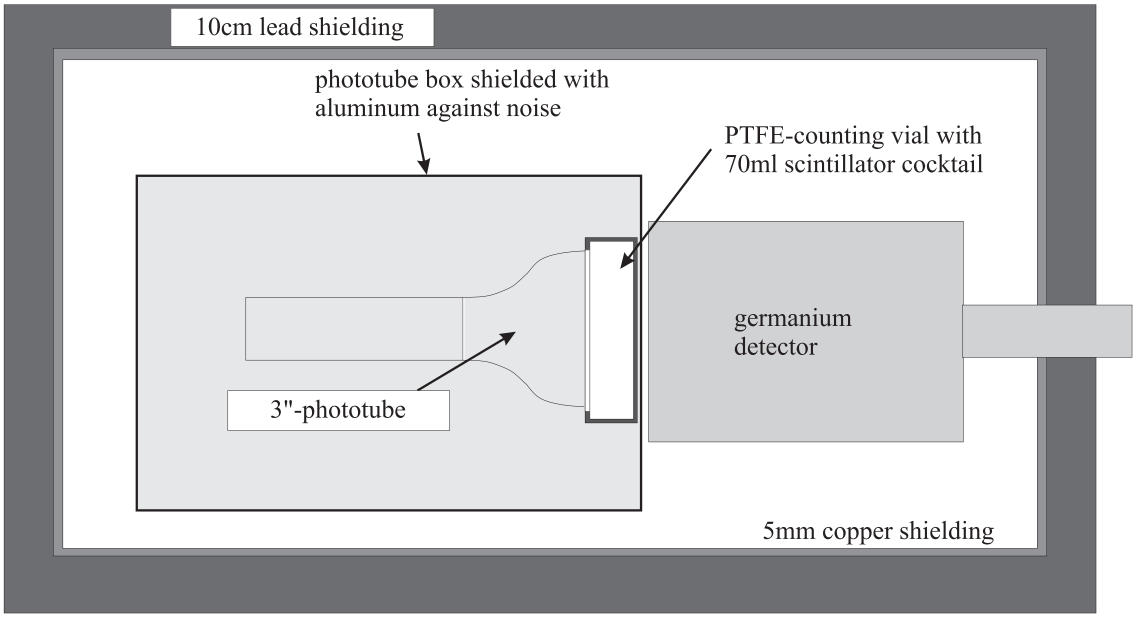

Figure 2: *Setup for coincidende measurements with β's or conversion electrons.*

Counting: The acidic phase was counted directly at the endcap of a 150% HPGe-detector

without any coincidence mode. Because of the close distance to the detector and the large detector mass an efficiency of approx. 5% could be achieved for the 1524 keV line of ^{42}K. The efficiency curve was determined with a QCY 48 reference solution from Amersham in the same geometry correcting for cascade effects. The counting of the scintillator cocktail was carried out with a LOAx germanium detector from EG&G Ortec, with a crystal diameter of 70 mm, which is especially suited to the detection of low energy gammas occuring in the decays of ^{239}Np (106 keV), ^{233}Pa (312 keV) and ^{177}Lu (208 keV). As described in a previous paper in detail an isomeric state of ^{239}Pu populated in the decay of ^{239}Np can be used to improve the signal/background-ratio in the determination of ^{239}Np [4]. Because of the bad time resolution of the LOAx-detector, a delayed β-e$^-$-γ-coincidence was used, recording energy information of the γ, β and conversion electron, and time difference between the β and the conversion electron event by event with a CAMAC-DAQ. The set-up for the measurement is shown in Fig. 2. The signals of β's and conversion electrons in the scintillator are detected with a phototube with high efficiency.
For the determination of ^{233}Pa and ^{177}Lu, a β-γ- coincidence was used to reduce the dominating external background. The counting time was up to five weeks to optimize the sensitivity for ^{233}Pa.

Tracer experiments: To determine the efficiency of the radiochemical procedure described above several tracer experiments were carried out for the interesting nuclides with PXE and PC based scintillators. In contrast to aqueous samples, organic sample spiking is more complex, because, for example, the chemical binding of uranium traces in real samples is unknown. One possibility might be metal-organic complexes. Therefore element standard solutions of U, Th, Lu and La were evaporated until dry and dissolved in 200 μl 7 M HNO_3. The acid was subjected to extraction with 2 ml TBP, which was previously washed with ultrapure water and acid. The TBP was dissolved in 100 ml PC and 100 μl of the mixture was added to the tracer samples in the irradiation flasks. Because K, Rb, Cd and In are difficult to transfer from nitric acid into TBP, these element standard solutions were diluted in methanol and the methanol was also added to the tracer samples. The concentrations of the tracer nuclides in the spiked samples were chosen between $10^{-9} - 10^{-6}$mol/l, because wall adsorption effects start to become significant within this concentration range.

To get the same liquid state after irradiation, the spiked samples were also irradiated for several days. There are two arguments why the initial chemical binding of the artificially added nuclides before irradiation might not be relevant and why these tracer experiments are therefore meaningful. Firstly, the strong degradation of the organic liquids during the irradiation process might cause a certain reset of the chemical binding, in which the interesting nuclides were present before irradiation and secondly, the single neutron capture process can change the chemical binding microscopicly. Nevertheless a systematic uncertainty remains.

After irradiation the same radiochemical procedure described above was applied to the spiked samples. For every step the efficiencies were determined by taking samples of the different solutions.

Results and discussion

Efficiency: The results of the tracer experiments are listed for PC based scintillators in Tab. 1 and for PXE based scintillators in Tab. 2. A few impurities were found in addition, so that efficiencies can be also studied for elements which have not been artificially added to the spiked samples.

The second column shows for both scintillator types that a major fraction of activated nuclides are adsorbed at the wall of the irradiation flasks with exception of Au. This fraction can be desorbed by rinsing the flasks with hot conc. HNO_3 twice for 1 min. In the PC of the first rinsing a minor part is desorbed. To control possible irreversible adsorption losses, the flasks were etched after the second rinsing with HF/HNO_3 and this solution was also counted. Upper limits of 10% were found for all tracer elements and the values or limits are significantly lower in many cases.

The fraction, which is not adsorbed at the wall, is distributed between the organic and the acidic phase after extraction. The absolute percentages are listed in column 3 and 4, the extraction yield in column 5. Because for some nuclides no positive signals are found in both phases, only lower limits can be given for their abundances in both phases taken together. The yields of the acidic extraction are lower than 0.5 only for ^{198}Au and ^{122}Sb. For ^{233}Pa, ^{239}Np and ^{140} La lower extraction yields than those listed have been observed for

Table 1: *Distribution of activated tracer nuclides in spiked PC samples. A major fraction is found to be adsorbed at the wall, but can be desorbed by rinsing with hot conc. HNO_3. From the other fraction a major part can be extracted with 5% HNO_3 for some elements. For ^{177}Lu and ^{114}In no positive signal was found in the acidic and organic phase.*

	desorbed fraction from wall	acidic extraction acid. phase	organ. phase	yield of acid. extraction	total yield
^{239}Np	80 %	11 %	6 %	0. 67	91 %
^{233}Pa	75 %	20 %	≤5 %	≥0. 8	≥ 96 %
^{177}Lu	≥95 %	≤5%	—	≥95 %	
^{140}La	93 %	4 %	2 %	0. 67	97 %
^{114}In	≥56 %	≤44%	—	≥56 %	
^{24}Na	38 %	50 %	12 %	0. 8	88 %
^{99}Mo	25 %	50 %	25 %	0. 67	75 %
^{69}Zn	61 %	≥31 %	≤8 %	≥0. 8	≥92 %

Table 2: *Distribution of activated tracer nuclides in spiked PXE samples. A major fraction is found to be adsorbed at the wall, but can be desorbed by rinsing with hot conc. HNO_3. From the other fraction a major part can be extracted with 5% HNO_3 for some elements. For ^{177}Lu, ^{42}K, ^{115}Cd, ^{114}In and ^{86}Rb no positive signal was found in the acidic and organic phase.*

	desorbed fraction from wall	acidic extraction acid. phase	organ. phase	yield of acid. extraction	total yield
^{239}Np	61-66 %	30-33 %	≤9 %	≥0. 75	≥ 91 %
^{233}Pa	66-79 %	18-21 %	≤15 %	≥0. 55	≥84 %
^{42}K	≥79 %	≤21%	-	≥79 %	
^{177}Lu	≥84 %	≤16%	-	≥84 %	
^{140}La	88 %	8 %	4 %	0. 67	96 %
^{115}Cd	≥83 %	≤17%	-	≥83 %	
^{114}In	≥80 %	≤20%	-	≥80 %	
^{86}Rb	≥75 %	≤25%	-	≥75 %	
^{69}Zn	43 %	47 %	10 %	0. 82	90 %
^{198}Au	20 %	10 %	70 %	0. 13	30 %
^{122}Sb	45 %	11 %	44 %	0. 20	56 %

shaking times between 5-10 min. It is therefore important to keep the shaking time strictly to 15 mins. Because 150 ml instead of 100 ml are used for real samples, the listed extraction yields are conservative. Taking the numbers of column 2 and 3 together, the total yield is obtained before the concentration of all acidic fractions, which has lower limits of over 75% for all radionuclides listed above for PXE-scintillators. For PC-scintillators lower limits of the total yield are only below 75% for In, whereas all other nuclides have 75% and better.
On the other hand the high total yields are only relevant if the fraction of adsorbed nuclei is similar in real samples. This might be not valid if the radioactive impurities are contained in microparticles. In this case a distribution according to the volume ratio of the acidic and organic phase is more realistic. This would lead to total yields of about 50% instead of over 80%. To avoid an overestimation of efficiency the results were therefore first calculated with 100% and then corrected with 0.75. With a given error of 50% both scenarios are included. For ^{198}Au and ^{122}Sb the listed total yields are used.

The efficiencies for the wet ashing procedure only show a result significantly below 100% for ^{233}Pa. A yield of 30% is reproducibly obtained for this nuclide, whereas the remaining fraction can only be dissolved with HF.
The efficiencies for the TBP-extraction are known for many elements [5], but were also tested in the tracer experiments. Distribution coefficients D were only determined as being close to 1 for for ^{198}Au ($D \approx 1$) and ^{239}Np ($D \approx 3$).

There is no better cross check of an analysis method than a confirmation with an independent method. The prototype detector CTF of BOREXINO has a sensitivity for ^{226}Ra and ^{228}Th of 10^{-16}g/g expressed in U- and Th-equivalent [4]. For a PXE-sample analyzed with both methods, a good agreement of the results was obtained for U and Th under the assumption of equilibrium in both chains.

Sensitivity: The detection limits and blank ranges for several elements obtained so far are listed in Tab. 3. For , for which no tracer experiments were carried out so far, an efficiency of 100% corrected with 0.75 is assumed. The given range for each element is determined by the results of the three most sensitive measurements. The results show, that high sensitivity can be obtained with the described NAA method for many elements and that is possible to

Table 3: *Detection limits and ranges of blank values of the described NAA method in [g/g].*

element	detection limit	range of blank values	element	detection limit	range of blank values
Ag (^{110}Ag	$3 \cdot 10^{-13}$	$\leq 3-4 \cdot 10^{-13}$	La (^{140}La)	$1 \cdot 10^{-15}$	$6-10 \cdot 10^{-15}$
Au (^{198}Au)	$3 \cdot 10^{-16}$	$\leq (7-10) \cdot 10^{-16}$	Lu (^{177}Lu)	$4 \cdot 10^{-16}$	$\leq (4-10) \cdot 10^{-16}$
Ca (^{47}Ca)	$1 \cdot 10^{-10}$	$\leq 1-7 \cdot 10^{-10}$	Mo (^{99}Mo)	$4 \cdot 10^{-13}$	$\leq 4-5 \cdot 10^{-13}$
Cd (^{115}Cd)	$1 \cdot 10^{-13}$	$\leq (1-8) \cdot 10^{-13}$	Na (^{24}Na)	$3 \cdot 10^{-14}$	$1-30 \cdot 10^{-12}$
Ce (^{141}Ce)	$1 \cdot 10^{-13}$	$\leq 1-3 \cdot 10^{-13}$	Rb (86Rb)	$5 \cdot 10^{-13}$	$\leq (5-15) \cdot 10^{-13}$
Co (^{60}Co)	$2 \cdot 10^{-14}$	$2-10 \cdot 10^{-14}$	Sb (^{122}Sb)	$4 \cdot 10^{-15}$	$2-8 \cdot 10^{-14}$
Cr (^{51}Cr)	$1 \cdot 10^{-13}$	$5-40 \cdot 10^{-13}$	Sm (^{153}Sm)	$6-30 \cdot 10^{-15}$	$6-30 \cdot 10^{-15}$
Fe (^{59}Fe)	$1 \cdot 10^{-11}$	$\leq (1-3) \cdot 10^{-11}$	Th (^{233} Pa)	$2 \cdot 10^{-15}$	$\leq (2-5) \cdot 10^{-15}$
In (^{114}In)	$4 \cdot 10^{-13}$	$\leq (4-12) \cdot 10^{-13}$	U (^{239}Np)	$2 \cdot 10^{-16}$	$\leq 2-20 \cdot 10^{-16}$
Ir	$1 \cdot 10^{-14}$	$\leq (1-2) \cdot 10^{-14}$	W	$1 \cdot 10^{-14}$	$2- \leq 6 \cdot 10^{-14}$
K	$2 \cdot 10^{-12}$	$3-20 \cdot 10^{-12}$	Zn	$3 \cdot 10^{-13}$	$3-20 \cdot 10^{-12}$

get ultrapure liquid organic scintillators. A detailed description of purities of commercially available scintillator components and possible methods for a further purification is given in a paper under preparation. The sensitivity is limited by different reasons. For all elements with limits for the range of blank values (Cd, Fe, In, Ir, Lu, Rb and Th) it can be improved by increasing neutron flux, sample mass, background of measurement etc.. Positive signals for Ag, Au, Ca, Ce, Co, Cr, K, La, Mo, Na, Sb, Sm, U, W and Zn are probably blank values, at least partly. This is concluded from measurements of several different samples, which reveal similar results for these elements. Sample contamination from dust during sample preparation or diffusion of impurities from the irradiation flask into the sample during irradiation are the most likely explanations. Results of presently performed measurements of ultrapure water with irradiation flasks of different purities show for K and Na a significant correlation with the purity of the flask. In addition an increase of Na- and K-contents in the analyzed water is obtained by longer irradiation times, which excludes sample handling before irradiation as the dominating blank source for these elements. To avoid possible sample contamination from irradiation flasks made of synthetic quartz a new irradiation flask made of single crystal silicon was fabricated last year and is presently tested with irradiations of ultrapure water. First results are presented in this conference [2]. Because it is very difficult to determine the blank values without

Table 4: *Taking the sensitivity for the radionuclides upper limits for achievable background rates in liquid organic scintillators can be deduced. For uranium and thorium equilibrium in the decay chains is assumed and only β-emitters are taken into account. The values are given in counts/day/ton.*

element	background rate	element	background rate
K	8 - 53	La	$(4\text{-}7)\cdot 10^{-4}$
Rb	40 - 120	Lu	$(2\text{-}4)\cdot 10^{-3}$
Cd	$(1\text{-}11)\cdot 10^{-5}$	Th	4-9
In	$(9\text{-}26)\cdot 10^{-3}$	U	1-10

As far as the reproducibility is concerned a factor of 2 or better is achieved for nearly all elements, which are significantly above the blank region. Nevertheless an improvement of the radiochemical procedure is worth striving for to exclude possible systematic errors. An counter current extractor will be used for the acidic extraction instead of a separatory funnel to increase the extraction efficiency close to 100% for all elements. For the subsequent steps the addition of K-, La-, Lu-, Cd-, In-, Rb-carrier solutions will be considered to determine the chemical yield for these steps in every sample.

The achieved sensitivities for U, Th, K and the other naturally occuring radionuclides, for which the developement was mainly carried out, show, which upper limits can be realized for the background rates from these elements in organic liquid scintillators. They are listed in Tab. 4.

Summary

A NAA method was presented, which allows the sensitive determination of K, Th, U and other trace impurities in liquid organic scintillators. 250 ml samples are irradiated up to 120 h at a neutron flux of $5\text{-}8\cdot 10^{12}\,cm^{-2}s^{-1}$. To increase sensitivity for the interesting nuclides acidic extraction, wet ashing and TBP-extraction were applied after irradiation for radiochemical separations. Tracer experiments show an efficiency over 75% of the chemical procedure after irradiation for ^{239}Np, ^{42}K, ^{177}Lu, ^{140}La, ^{115}Cd, ^{114}In and ^{86}Rb. A much lower total efficiency of 27% is only obtained for ^{233}Pa. A further improvement of the procedure is therefore especially necessary for this nuclide. Counting is carried out with HPGe-detectors of high efficiency and especially for ^{239}Np coincidence techniques improve

the signal/background-ratio significantly, close to a factor of 10^4. The sensitivity is partly dominated by blank values, which will be reduced by a new irradiation flask made of single crystal silicon. For other elements such as Th, Lu, Cd, In and Rb a new low background laboratory at Garching will improve the detection limits for these elements.

The sensitivity obtained so far for U, Th, Lu, La, Cd and In is sufficient for the solar neutrino experiment BOREXINO. Only for K and Rb further improvement is needed. Because the BOREXINO-experiment has the highest radiopurity requirements of existing and proposed experiments, the presented NAA method is a helpful tool for low background experiments in physics.

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