New records on low activity measurements with neutron activation analysis

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A very sensitive NAA technique of liquid organic scintillators has been developed at the Technische Universität München focusing on quasistable radionuclides. Combining important input factors for sensitive NAA very low detection limits are obtained, e.g. $2 \cdot 10^{-16} g/g$ for ^{238}U. This article describes these input factors and how they have been realized for the NAA of liquid organic scintillators. The results are discussed in the context with the solar neutrino experiment BOREXINO, for which this work has been started. Possibilities for a further improvement of sensitivity are presented as an outlook.

1. INTRODUCTION

What is the uranium content in single crystal silicon? A common answer even from specialists in the low background field is 'nothing'. Besides the fact, that this statement is wrong from an epistemological point of view, it shows that even the most sensitive analytical techniques cannot probe the impurity level of certain elements in very pure materials as silicon. What is the motivation for improving the sensitvity of these techniques?

Besides the general interest to push down the detection limits, semiconductor industry is one example where sensitive analytical techniques are important. Silicon and processing liquids have to be very pure and the purity requirements may increase in the future.

Not surprisingly also very high interest arises from fundamental physics, especially from weak interaction experiments in the low energy range. Low signal rates and radioactivity as a background source lead to very high requirements for the radiopurity of detector components. From a series of forthcoming neutrino experiments as Superkamiokande, SNO and Chooz, the solar neutrino experiment BOREXINO[1] requires the lowest limits for radioactive impurities, e.g. $10^{-16} g/g$ for uranium and thorium and $10^{-14} g/g$ for potassium in the liquid organic scintillator used for the detection of neutrinos.

2. INPUT FACTORS FOR SENSITIVE NAA

Neutron activation analysis (NAA) techniques have been developed at the Technische Universität München to approach these challenging numbers[2]. NAA is an absolute, sensitive analytical technique, where the sample is exposed to a neutron flux converting nuclides partly in instable nuclides by neutron reactions. The decays of these nuclides are counted afterwards, usually using characteristic gamma-lines, and a quantitative result is obtained for the content of impurities in the sample.

Obviously only a combination of all input factors for sensitive NAA leads to the best detection limits. Figure 1 shows the important factors.

Starting with the sample, it is evident, that materials are specially suited for NAA, if the matrix is not activated very strongly. This is usually the case, if the matrix irradiation produces nuclides with halflives much shorter than those of the interesting nuclides or if the branching ratio to excited states followed by $\gamma's$ is very low. H,C,N,O,Si and F are elements, which fulfill these requirements for most of the interesting impurities. Therefore water, quartz, silicon and many organics are very suited for NAA from this point of view.

A serious limitation for water and organics can arise from pressure build-up due to radiolysis dur-

Figure 1. Important input factors for sensitive NAA. For further descripition see text.

ing irradiation in closed irradiation vessels. How the pressure build-up can be avoided is discussed in another paper[2].
A big advantage of NAA is the compared to other analytical methods reduced cleanliness problem. For any sample treatment after irradiation usual sources of contamination, which arise from dust, processing chemicals or other sources are negligible, because they do not usually contain activated nuclides. For the NAA of solid samples any possible contamination before irradiation is also often irrelevant, because the surface can be etched afterwards removing the contamination. As for pure liquids the situation is of course totally different and the usage of pure laboratory tools (e.g. made out of teflon or quartz) as well as careful sample treatment in clean rooms or boxes is crucial before irradiation.
A very important factor for the sensitivity obtained is the irradiation. Irradiation time, sample mass and neutron flux should be optimized. But normally there are exogenous limitations due to the available reactor, irradiation facility and halflife of the interesting nuclides.
After irradiation and a certain 'cooling time' the sample is often measured without major treatment, because the good energy resolution of germanium detectors allows a multielement analysis without chemical separation methods. If however the compton background of interfering nuclides is limiting or coincidence techniques with $\beta's$ or conversion electrons have to be applied for an improvement of the detection limit, the application of radiochemical methods is necessary.
The final step is the measurement of the sample. To obtain a good sensitivity the detector efficiency is of course very important. For some elements specific coincidence techniques can be applied improving the signal/background ratio. A very simple $\beta-\gamma-$coincidence is useful for nearly all elements, if the external background of the germanium system is dominating. The only requirement is, that the β can be detected in a liquid scintillator. This can be achieved by decom-

posing or extracting the sample. The detection efficiency for the β in a scintillator is usually very high and the total efficiency is not reduced very much using this coincidence, while the external $\gamma-$background is suppressed significantly.
To obtain very low detection limits ultra low background γ-spectroscopy provides a new promising technique. On the other hand this technique is only useful, if the activity of the sample is very low or if interfering nuclides in the sample have been removed by radiochemical methods. Whereas in the last years radiochemistry was generally decreasingly used for NAA, the combination with ultra low background $\gamma-$spectroscopy could reinforce the application of radiochemical methods.

3. NAA OF LIQUID SCINTILLATORS

For the analysis of liquid scintillators for BOREXINO several points listed above have been realized. A detailed description of the applied procedures will be given in a paper under preparation, but the main aspects are shown in this section.
The scintillator samples are filled without preconcentration in 250ml irradiation flasks out of synthetic quartz, which have been soaked for several days in freshly subboiled HNO_3 and ultrapure water. The complete handling before irradiation is carried out in a class 10 clean box.
The irradiation time is up to 6 days at a thermal neutron flux of $8 \cdot 10^{12} cm^{-2} sec^{-1}$. A pressure build-up due to radiolysis of the scintillator is avoided by using an open irradiation vessel, so that the produced gas can escape. Because of the radiolysis the scintillator is severely degraded after irradiation and has lost its scintillation properties. For the application of coincidence techniques with $\beta's$ or conversion electrons and chemical separation of interfering nuclides, the scintillator is subjected to acidic extraction with 5% HNO_3 twice. The acidic phase with the activated ionic impurities is concentrated. Organic traces in this concentrated acid are removed by wet ashing. The residue of the ashing is dissolved in HNO_3 and the HNO_3 is extracted with tri-butylphosphate (TBP). Potassium and many other metals stay in the acidic phase, whereas neptunium and protactinium, which are used for the determination of uranium and thorium, are transferred to the TBP, which is mixed with a commercial scintillator cocktail for counting. The acidic sample is counted with a very big germanium detector of 150% efficiency, which is especially useful for the detection of the high energetic potassium line. The scintillator is measured with a germanium detector for the detection of $\gamma's$ and simultaneously with a phototube for the detection of $\beta's$ for coincidences. In the case of ^{239}Np a delayed $\beta - e^- - \gamma-$coincindence is used, for ^{233}Pa just a $\beta - \gamma-$coincidence to reduce the external background. The background suppression due to the delayed coincidence is more than 10^4 and neptunium can be detected nearly background free.
The efficiencies for the radiochemical procedures and the coincidences are determined by tracer experiments.

4. RESULTS AND DISCUSSION

Table 1
Detection limits for natural radioactive elements obtained with NAA of liquid organic scintillators in g/g. For comparison the required purity levels in BOREXINO are listed in the right column.

	NAA	BOREXINO
uranium	$2 \cdot 10^{-16}$	$1 \cdot 10^{-16}$
thorium	$5 \cdot 10^{-15}$	$3 \cdot 10^{-15}$
potassium	$3 \cdot 10^{-12}$	$4 \cdot 10^{-14}$
lanthanium	$2 \cdot 10^{-14}$	$6 \cdot 10^{-12}$
lutetium	$5 \cdot 10^{-14}$	$2 \cdot 10^{-14}$
cadmium	$7 \cdot 10^{-13}$	$1 \cdot 10^{-8}$
indium	$2 \cdot 10^{-12}$	$1 \cdot 10^{-11}$
rubidium	$1 \cdot 10^{-11}$	$2 \cdot 10^{-13}$

The presently achieved detection limits are listed in Table 1. The limitation for the several elements are caused by different reasons. For potassium a positive signal is obtained, but from a series of irradiations it can be concluded, that the

signal is dominated by blank. The origin of the blank could be contamination of the scintillator by the handling before irradiation or by the vessel or pool water during irradiation. It is difficult to measure the blank independently. The analysis of the purest available liquid gives therefore an upper limit for the detection limit of potassium. For thorium the limitation is caused by the external background of the used germanium detector setup, whereas the detection limit for uranium can be only improved by increasing the activation potential (higher neutron flux or sample mass) or a more efficient detection method.
Concerning the requirements for BOREXINO Table 1 shows that the achieved detection limits are sufficient for cadmium, indium, and lanthanum, close to the required limits for lutetium,uranium and thorium and still two orders of magnitude too high for potassium and rubidium.
The attentive reader may have noticed that the number for the acceptable impurity level of thorium in BOREXINO is inconsistent with the number given in the introduction. The discrepancy comes from the necessity to look at the uranium and thorium chains more closely. The numbers of $10^{-16}g/g$ are given for equilibrium in both chains, which cannot be expected after several chemical processes during the production of the scintillator components. Therefore NAA, which is only sensitive to quasistable nuclides, can only test the first part of both chains, which have to be in equilibrium and for which the numbers of Table 1 are relevant. Lower parts, starting from ^{226}Ra and ^{228}Th are directly measured with a prototype detector of BOREXINO in the Gran Sasso underground facility (Italy) using 5t of scintillator shielded by 1000t of ultrapure water. The described NAA techniques are therefore complementary to the prototype detector and will be important to check the purity of the BOREXINO scintillator.

5. OUTLOOK AND CONCLUSIONS

The presented combination of important input factors for sensitive NAA shows which detection limits and purity levels of radioactive elements can be achieved in organic scintillators. This might be helpful for the design of other ultra low background experiments. How these purity levels can be obtained in organic scintillators will be discussed in a paper under preparation.
Even though the detection limit for uranium is to our knowledge far below existing numbers for organic materials, further improvement for uranium and the other elements should be feasible by eliminating the limiting factors.
A new irradiation vessel out of single crystal silicon will solve the problem of a possible sample contamination by the used synthetic quartz vessels, because the purity of single crystal silicon is much higher than that of synthetic quartz. A new low background laboratory at the Physik Department of the Technische Universität München close to the research reactor will improve the detection limits for nuclides, which are dominated by the external background.
For uranium a further increase of sensitivity seems to be possible using a delayed $\beta - e^- -$coincidence. This would require a better radiochemical separation method and probably pulse shape analysis. The higher detection efficiency compared to the presently used delayed $\beta - e^- - \gamma -$coincidence could lead to a detection limit of $10^{-17}g/g$.

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REFERENCES

1. BOREXINO Coll., Borexino Proposal, 1991, INFN Milan. - Addendum to the Borexino Proposal, July 1996, INFN Milan.
2. T. Goldbrunner et al., to be published winter 96/97 in J. of Radioanalytical and Nuclear Chemistry, proc. of MTAA-9 Seoul 1995.