Neutron Activation Analysis of Ultrapure Water in a 500 ml Silicon Single Crystal Irradiation Flask

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Trace element analysis of ultrapure liquids requires the avoidance of contamination not only during preparation but also during irradiation of the sample. Double subboiling distilled water activated within flasks made out of synthetic quartz shows a significant correlation between irradiation time, quality of the flasks and the determined trace element concentration. The resulting falsification of the analysis and limitation of sensitivity seems to be caused by diffusion-like processes during irradiation.
Even though single crystal FZ-silicon is rather brittle, it has been possible to fabricate a 500 ml irradiation flask out of this extremely pure material. The flask as well as its application in the analysis of double subboiling distilled water are discussed in the article.

Introduction

New detectors in neutrino and astroparticle physics, e. g. the solar neutrino experiment BOREXINO [1], are based partly on an extremely high radiopurity of their detector components. These purity demands are necessary, for otherwise the weak signal to be detected would completely be covered by natural radioactivity. At BOREXINO the tolerable limit for the potassium concentration in the liquid organic scintillator amounts to 10^{-14} g/g; the concentrations of uranium and thorium have to be lower than 10^{-16} g/g. NAA is sensitive enough to determine such ultra-traces in case all parameters regarding the signal-to-noise ratio are optimized [2]. Specifically, the irradiation time has to exceed several days in our case and any contamination of the sample must be excluded during both preparation and irradiation.
This paper compares the analysis of double subboiling distilled water, in the case where the irradiation is carried out in a synthetic quartz flask and in a silicon irradiation flask. The uncertainty in all of the data is about 30 % (1 σ)

Experimental

Irradiation in the Synthetic Quartz Flask

Water samples are prepared in the following way: Deionized water (Milli-Q) is distilled twice in a subboiling device made out of ordinary quartz. The flasks are soaked with nitric acid (5%) and subboiling distilled water for several days before use. The water sample is subboiled directly into the flask or stored for short periods in a PFA-bottle. All the handling of the samples is carried out in a class 1 - 10 clean box. After irradiation, the water sample is concentrated by use of a surface evaporator. The irradiation flask is rinsed with 20 ml HNO_3 (7M) for about 5 minutes in order to remove plated ions from the flask´s surface. The rinsing is added to the sample.

Irradiation in the Silicon Flask

Water samples irradiated in the silicon flask are prepared in the same way as for the quartz samples: Deionized water (Milli-Q) is double subboiling distilled and filled directly (via PE-pipette) into the irradiation flask. The flask is soaked with nitric acid (5%, subboiling distilled) and subboiling distilled water for several days before being filled with the sample water.

The handling of the samples is carried out in a class 1 - 10 clean box. After irradiation the water samples are reduced by use of a surface evaporator. The irradiation flask is rinsed with 20 ml HNO_3 (7M) for about 5 minutes to remove plated ions from the flask´s surface. The rinsing is added to the sample.

Fabrication of the Silicon Flask

The silicon flask and its top have been fabricated of single crystal FZ-silicon, the outer irradiation container is made out of synthetic quartz (figure 1). The outer irradiation container gets put over the flask and its top so that pool-water can´t get into the sample [3]. During irradiation the pool-water surface is located about five centimeters below the upper edge of the flask. As organic liquids as well as water decompose during irradiation, there are two holes in the top of the flask so that gases can escape. Via these holes gases can also be exchanged between the sample liquid and the pool-water.

Impurities on the flask´s surface stemming from the fabrication process are removed by wet etching methods. To prevent recontamination only subboiling distilled acids are used. After the removal of the silicon oxide the bulk material is etched by a mixture of HF(48%) / H_2SO_4(97%) / HNO_3(65%) in a volumetric ratio of 1/3/10, which corresponds to an average etching ratio of about 4 µm/min.

During etching the surface is sprinkled with nitrogen to reduce the formation of etching dimples. These enlarge the surface and all effects associated with it. The removal of a 200 µm surface layer is sufficient to remove impurities caused by fabrication. Figure 2 shows the silicon surface before etching and after the removal of 130 µm surface layer.

Analysis of Silicon

For a selective separation of background-producing isotopes a sample of the silicon used for the fabrication of the flask has been dissolved after irradiation.

The selective extraction of ^{24}Na by hydrated antimony pentoxide (HAP [4]) improves the sensitivity for short-lived isotopes such as ^{42}K or ^{194}Ir. In long-time irradiations of undoped silicon the pure β^--emitter ^{32}P ($T_{1/2}$ = 14.26 d; $E_\beta \leq$ 1.7 MeV) is produced mainly via the succeeding capture of two neutrons by ^{30}Si and the intervening decay of ^{31}Si. Bremsstrahlung and therefore background is reduced effectively by precipitation and separation of phosphorus as zirconium phosphate. The yield of both radiochemical separation procedures is tested by tracer experiments with silicon samples of very high impurity. For the determination of uranium special coincidence techniques have been developed. A detailed description of the radiochemical and coincidence techniques can be found in the references [5, 6].

Results

Irradiation in the Synthetic Quartz Flask

Table 1 shows the impurities [g/g] that have been determined in double subboiling distilled water. The water was irradiated in two different flasks (flask I, flask II) and at different irradiation times.
Flask I has been irradiated only several hours before and has been fabricated in a way that avoids the entry of impurities during fabrication. Bulk impurities of flask II differ significantly from flask I, besides flask II has already been activated for several hundred hours before.
The concentrations of trace elements correlate both with irradiation time and with the quality and purity of the irradiation flask in use. The flask I-measurements reveal a correlation between trace element concentrations and irradiation time only for sodium and potassium, whereas long-time irradiations in flask II indicate a more general effect: Compared to one-hour irradiations in flask I the concentrations of sodium and potassium change at least two orders of magnitude; iridium, lanthanum, antimony and tungsten are also altered significantly. Short-time irradiation data of flask II (not included in table 1) behave correspondingly, i. e. are lower than long-time irradiation data of flask II but higher than short-time irradiation data of flask I.
According to these observations the use of irradiation flasks made out of synthetic quartz can limit the sensitivity in the analysis of ultrapure liquids.

Trace Elements in Silicon

The easiest way to avoid that impurities come out of the irradiation flask and falsificate the analysis of ultrapure liquids is just to use material with a lower impurity concentration. In the silicon single crystal used for the fabrication of the irradiation flask positive values can be determined only for few elements (table 2).
Single crystal FZ-silicon exceeds the purity of synthetic quartz (see table 1) considerably for most elements.

Irradiation in the Silicon Flask

Table 3 shows trace concentrations found in water at different irradiation times using the silicon irradiation flask.
In contrast to the flask made out of synthetic quartz, there is no significant correlation between irradiation time and the determined impurity concentration for the silicon flask (see discussion).

Discussion

The discussion concentrates on the deviations in the determination of potassium and sodium in the water samples.

Synthetic Quartz Flask

Potassium and sodium constitute the main impurities in the flask (besides calcium). As these elements also correlate most strongly with irradiation time and the flask´s quality, it is natural to suppose diffusion-like effects: At 65°C (sample temperature

due to irradiation) diffusion constants of sodium and potassium in quartz have to be obtained by extrapolation from measurements at 1000°C [7, 8].
Calculations show that ordinary diffusion is insufficient to explain the quantity of the observed effect by approximately two orders of magnitude. Nevertheless irradiation time and the quality of the irradiation flask seem to have a definite influence on the analysis. In particular, bombardment with neutrons and prompt γ´s might increase diffusive effects during irradiation and alter the microscopic structure of a flask´s surface such that diffusion becomes more facilitated.

Silicon Flask

As the wall of the silicon flask contains much lower concentrations of sodium and potassium, diffusion-like effects should be suppressed:
Using the silicon flask, the concentration of sodium stays constant (table 3) and the ramping of the concentration of potassium can be explained quantitatively by the interference of argon (see below). As the 48h-irradiation-sample has been purged with helium before irradiation, the argon concentration of the sample and therefore the detected potassium concentration is reduced.
The sodium concentration is increased by one order of magnitude compared to the most sensitive quartz flask analysis, This can be understood if ^{24}Na in both cases stems from the ^{28}Si(n,αp)^{24}Na-reaction within the flask's wall. The silicon flask does not only have a higher silicon concentration, but also a larger surface due to the etching procedure described in the experimental section.
Besides the high concentration of lanthanum (t_{irr} = 48 h) there is no significant discrepancy between the silicon flask data and the most sensitive quartz flask results. It can not be excluded that purging with helium is a source of contamination causing the remarkable increase in the concentration of lanthanum.

^{28}Si(n,αp)^{24}Na

^{24}Na is produced in quartz-made or silicon-made flasks by fast neutrons (E_n > 14.7 MeV) via ^{28}Si(n,αp)^{24}Na (σ_{fast} = 1.8 10^{-9} b) [9], even if the flasks originally don't contain any sodium at all. This exothermic reaction does not only create ^{24}Na but also can transport it by recoil into the sample. As the energy dependence of the cross section is not known, one only can estimate very roughly the resulting detection limit for the liquid sample. In the case where

- ^{28}Si(n,αp)^{24}Na is resonantly induced by neutrons of energy X [MeV],
- the surplus energy (X - 14.7 MeV) is completely converted into kinetic energy of ^{24}Na,
- ^{24}Na nuclei with kinetic energy of 1 MeV move about 2.2 μm in quartz [10],
- ^{28}Si(n,αp)^{24}Na leads to a detection limit of 2 10^{-10} g/g for sodium in quartz,
- the inner surface of the quartz flask amounts to about 200 cm^2,
- the density of quartz is about 2.7 g/cm^3

the detection limit for sodium in the liquid sample should be about

$$(X[MeV] - 14.7)\ 5 \cdot 10^{-14} \text{ g/g.}$$

This mechanism doesn´t cause an irradiation-time dependent falsification of the sample's sodium concentration and should not depend significantly on the quality of the flask's wall

Interference between Argon and Potassium

^{42}K is produced not only by neutron capture of ^{41}K or other well known exchange reactions with calcium and scandium, but also by the capture of two neutrons by ^{40}Ar and the intervening decay of ^{41}Ar. This second order effect becomes important if there's a big difference between the concentration of argon and potassium in the sample. The argon content in liquids is quite high, about 4 10^{-7} g/g in water and about 10^{-6} g/g in organic liquids. Double excitation causes a non linear time-dependent effect, but can not fully explain the increase of the potassium concentration in table 1. An argon concentration of 4 10^{-7} g/g leads to a blank value of about 5 10^{-15} g/g at an irradiation time of one hour and of about 6 10^{-12} g/g at 96 hours [6].

In principle, the presence of ^{24}Na can arise from neon via the same mechanism, but the isotopic ratios of the nuclei involved reduce the power of the effect by approximately two orders of magnitude. In addition neon is a rather rare noble gas, so the effect should be negligible at concentrations examined so far.

Conclusion

NAA of double subboiling distilled water shows that the sensitivity of the analysis can be limited by impurities within the irradiation flask even if a high quality material such as synthetic quartz is used.

Further experiments will be undertaken, for example, to identify unambigously the provenience of the sodium determined in the water. The ^{28}Si(n,αp)^{24}Na-reaction can be suppressed at an irradiation position, where the flux of fast neutrons is strongly reduced, e. g. at a heavy water reactor.

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Tables

Table 1: Trace impurities [g/g] in double subboiling distilled water. The first two data-columns have been determined by activation in flask I lasting 1 h or 23 h respectively. The bulk impurities of this flask are quoted in the third data-column. An irradiation of 96 h has been carried out in an irradiation flask with lower quality (flask II, data-column four and five).

	Conc. in Water	Conc. in Water	Conc. in Flask I [g/g]		Conc. in Water	Conc. in Flask II [g/g]
	t_{irr}=1 h	t_{irr}=23 h			t_{irr}=96 h	
As	**< 4 10^{-14}**	**< 2 10^{-14}**	< 4 10^{-13}	As	**< 1 10^{-12}**	< 5 10^{-12}
Ca	**< 6 10^{-9}**	**< 2 10^{-9}**	2 10^{-7}	Ca	**3 10^{-9}**	1 10^{-6}
Cr	**< 1 10^{-11}**	**5 10^{-13}**	7 10^{-11}	Cr	**< 2 10^{-11}**	3 10^{-9}
Fe	**< 7 10^{-10}**	**< 3 10^{-11}**	5 10^{-9}	Fe	**2 10^{-11}**	1 10^{-7}
Ir	**< 2 10^{-14}**	**< 5 10^{-15}**	9 10^{-12}	Ir	**1 10^{-13}**	7 10^{-10}
K	**< 8 10^{-13}**	**3 10^{-12}**	8 10^{-9}	K	**8 10^{-11}**	6 10^{-7}
La	**< 2 10^{-14}**	**< 4 10^{-15}**	2 10^{-11}	La	**5 10^{-14}**	4 10^{-10}
Na	**1 10^{-13}**	**2 10^{-12}**	2 10^{-8}	Na	**9 10^{-11}**	2 10^{-7}
Sb	**< 6 10^{-14}**	**7 10^{-14}**	8 10^{-12}	Sb	**3 10^{-13}**	6 10^{-11}
W	**< 6 10^{-14}**	**2 10^{-14}**	< 7 10^{-13}	W	**8 10^{-13}**	1 10^{-10}
Zn	**< 7 10^{-12}**	**< 2 10^{-12}**	2 10^{-10}	Zn	**4 10^{-12}**	1 10^{-7}

Table 2: Impurities in FZ-silicon [g/g]. *The determination limit for sodium is caused by fast neutrons via $^{28}Si(n,\alpha p)^{24}Na$ (see also below).

Trace Element Concentration in FZ-Silicon [g/g]			
K	$< 2 \cdot 10^{-12}$	Hg	$< 2 \cdot 10^{-12}$
Na*	$5 \cdot 10^{-10}$	In	$< 3 \cdot 10^{-13}$
U	$< 3 \cdot 10^{-17}$	Ir	$< 8 \cdot 10^{-15}$
Th	$< 3 \cdot 10^{-16}$	La	$< 3 \cdot 10^{-15}$
Ag	$1 \cdot 10^{-15}$	Lu	$< 3 \cdot 10^{-16}$
As	$4 \cdot 10^{-13}$	Mo	$< 2 \cdot 10^{-12}$
Au	$< 2 \cdot 10^{-15}$	Os	$< 2 \cdot 10^{-15}$
Ba	$< 9 \cdot 10^{-14}$	Rb	$< 3 \cdot 10^{-14}$
Br	$< 4 \cdot 10^{-15}$	Ru	$< 5 \cdot 10^{-14}$
Cd	$< 5 \cdot 10^{-13}$	Sb	$4 \cdot 10^{-14}$
Co	$2 \cdot 10^{-15}$	Sc	$< 1 \cdot 10^{-17}$
Cr	$6 \cdot 10^{-13}$	Se	$< 1 \cdot 10^{-13}$
Cs	$< 2 \cdot 10^{-15}$	Ta	$< 6 \cdot 10^{-14}$
Cu	$< 3 \cdot 10^{-12}$	W	$< 1 \cdot 10^{-14}$
Fe	$< 2 \cdot 10^{-13}$	Zn	$< 3 \cdot 10^{-15}$
Ga	$< 7 \cdot 10^{-14}$	Zr	$< 6 \cdot 10^{-14}$

Table 3: Impurity concentrations [g/g] found in ultrapure water using a silicon irradiation flask. Irradiation time varies between one hour and 48 hours.

	Conc. in Water [g/g]		
	1 h	42 h	48 h
As	$< 4\ 10^{-14}$	$4\ 10^{-14}$	$2\ 10^{-14}$
Ca	$< 4\ 10^{-9}$	$< 7\ 10^{-11}$	$< 2\ 10^{-10}$
Cr	$< 4\ 10^{-12}$	$5\ 10^{-13}$	$1\ 10^{-12}$
Fe	$< 2\ 10^{-10}$	$< 6\ 10^{-12}$	$< 2\ 10^{-11}$
Ir	$< 2\ 10^{-14}$	$< 4\ 10^{-15}$	$7\ 10^{-15}$
K	$< 3\ 10^{-12}$	$6\ 10^{-12}$	$4\ 10^{-12}$
La	$< 1\ 10^{-14}$	$< 2\ 10^{-15}$	$1\ 10^{-14}$
Na	$2\ 10^{-12}$	$2\ 10^{-12}$	$2\ 10^{-12}$
Sb	$< 7\ 10^{-14}$	$3\ 10^{-14}$	$6\ 10^{-14}$
W	$< 4\ 10^{-14}$	$1\ 10^{-14}$	$1\ 10^{-14}$
Zn	$< 6\ 10^{-12}$	$< 3\ 10^{-12}$	$<2\ 10^{-12}$