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**NUCLEAR  
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Section A

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# Novel technique for ultra-sensitive determination of trace elements in organic scintillators

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## Abstract

A technique based on neutron activation has been developed for an extremely high sensitivity analysis of trace elements in organic materials. Organic materials are sealed in plastic or high-purity quartz and irradiated at the HFIR and MITR. The most volatile materials such as liquid scintillator (LS) are first preconcentrated by clean vacuum evaporation. Activities of interest are separated from side activities by acid digestion and ion exchange. The technique has been applied to study the liquid scintillator used in the KamLAND neutrino experiment. Detection limits of  $<2.4 \times 10^{-15}$  g  $^{40}\text{K/g}$  LS,  $<5.5 \times 10^{-15}$  g Th/g LS, and  $<8 \times 10^{-15}$  g U/g LS have been achieved.

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## 1. Introduction

A next generation of nuclear and particle physics experiments will require increasingly pure materials for success. The signatures of extremely rare processes such as neutrino interaction and oscillation, double beta decay, and dark matter interaction are often masked by common terrestrial backgrounds. New underground facilities may

shield experiments from the background derived from cosmic radiation. However, isolating the physics processes from radiation in the experimental apparatus itself remains critical. Radionuclides such as uranium, thorium, and potassium-40 have long half-lives and remain abundant in the earth's crust. The decay products of these nuclei and their daughters can often have the same low-energy signatures of the rare processes studied. To enable experiments probing rare phenomena, new research into the selection of materials with very high purity in radionuclides is key.

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## 2. KamLAND physics and requirements

A prime example is the KamLAND experiment [1], which motivated this work. KamLAND, installed in the cavity of the concluded Kamiokande experiment in the Japanese Kamioka underground laboratory, is detecting neutrino oscillations in disappearance mode using Japanese nuclear power reactors as anti-neutrino sources [2]. Its long baseline gives KamLAND sensitivity to  $\Delta m^2$ -values in the range of the so-called large mixing angle solution of the solar neutrino problem. The flux weighted mean distance to 22 nuclear power stations in Japan and Korea is about 200 km. This large distance to the neutrino sources, which is essential for the physics, results in an extremely small anti-neutrino interaction rate of only about 2 per day in KamLAND's 1000 tons fiducial volume, consisting of organic liquid scintillator.

Owing to the low anti-neutrino energies, physics events can be masked by natural, anthropogenic and cosmogenic radioactivity. It has been estimated, that the concentrations of  $^{40}\text{K}$ ,  $^{232}\text{Th}$ , and  $^{238}\text{U}$  should not exceed  $10^{-14}$  g/g in order to not compromise the physics measurement [1]. As an example of the requirements in another organic material, concentrations of Th and U in the acrylic vessel of the Sudbury Neutrino Observatory (SNO) were measured to be less than the specified limits of  $10^{-13}$  g/g [3]. The goal of this work was therefore to test samples of the scintillation fluid for the presence of above elements at these very small concentrations.

## 3. NAA motivation

While direct radiation counting is the ideal analysis technique for radiation sensitive experiments, such analysis suffers from a lack of decay rate. As an example, at a concentration of  $10^{-14}$  g/g U, the expected decay rate is about 1 per day per 100 kg of sample. The large sample size needed therefore becomes impractical. At the same concentration a 1 kg sample contains about  $2.5 \times 10^{10}$  uranium atoms. Direct detection of this large population of parent nuclei can be achieved with inductively coupled plasma mass spectroscopy

(ICPMS) and neutron activation analysis (NAA). The secular equilibrium assumption in the uranium and thorium decay chains relate the parent population measurements to the expected radiation.

Using efficient ion sources, sensitivities to  $^{238}\text{U}$  of the required magnitude or even better have been reported in the literature [4]. However, these methods require the nuclides of interest to be in aqueous solution. Application of mass spectroscopy to organic liquids requires the blank free, efficient transfer of the elements of interest into aqueous solution. This in turn requires chemical manipulations before the analysis. The purity of the used chemicals is hence crucial for achieving a low blank reading. The basic principles governing trace element analysis by means of NAA have been worked out in great detail in the past. They shall hence not be discussed in this article. Textbooks such as Ref. [5] give a comprehensive overview. A further important criterion which led us to choose NAA as analysis tool was the fact that sensitivities even exceeding those required for our work have been reported in the literature [6], proving feasibility. Organic substances are, at least in principle, well suited for NAA. Hydrocarbons, consisting of C, H, N, O have no long-lived activation products. The nuclides of interest,  $^{41}\text{K}$ ,  $^{232}\text{Th}$ , and  $^{238}\text{U}$  on the other hand, offer sizable capture cross-sections and their activation products,  $^{42}\text{K}$ ,  $^{233}\text{Pa}$  and  $^{239}\text{Np}$ , have half-lives greater than 12 h, stable enough to allow decay radiation counting even after substantial shipping and processing delays.

A problem, however, arises from the fact that hydrocarbons tend to dissociate in a high neutron and gamma flux environment. This so called radiolysis leads to hydrogen outgassing inside the nuclear reactor used for the activation. In the previous work by the Munich group [6], pressure build-up in the sample containment vessel (and its potential rupture associated with sample loss) was prevented by venting the excess gas into the pool water of the reactor [7]. This approach has been used for liquid scintillator samples with up to 500 ml volume at the research reactor, FRM I, in Munich [8]. Detection limits of  $3 \times 10^{-12}$  g/g for K,  $2 \times 10^{-15}$  g/g for Th and  $2 \times 10^{-16}$  g/g for U have been reported in the literature [6]. More

recently, the Munich group obtained further improved sensitivities of  $1.8 \times 10^{-16}$  g/g for Th and  $1.0 \times 10^{-17}$  g/g for U [9]. The direct irradiation of liquid samples does not require extensive sample preparation or treatment prior to the analysis, enhancing the robustness against the introduction of unwanted contaminations. Although this procedure offers a number of positive features, its use seems to be limited to the research reactor facility in Munich. No research reactor could be found in the US which has an existing facility that would allow the irradiation of large liquid samples and the venting of potentially flammable gases into the coolant.

We therefore decided to develop a novel technique, not requiring the venting of excess gases. In the approach described here, the organic materials are gently heated in a clean vacuum chamber, in order to evaporate most of the organic until less than 1% by mass remains. Sample outgassing is substantially reduced, while most of the impurities survive evaporation and are analyzed in the residual organic. The sensitivities achieved with this new technique are not quite as stringent as those reported by the Munich group but, to the best of our knowledge, they are only exceeded by this group. The main advantage of the approach described in this article lies in the fact that it can be used at almost any research reactor, it does not require expensive, unique irradiation facilities, and it is therefore generally applicable. Irradiation facilities with very high neutron flux may also be used. At FRM I, the thermal neutron flux was limited to  $2 \times 10^{12}$ – $1.3 \times 10^{13}$   $\text{cm}^{-2} \text{s}^{-1}$ . By comparison, the thermal neutron flux available at the High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory and at the Massachusetts Institute of Technology Research Reactor (MITR) of MIT Nuclear Reactor Laboratory is with  $4 \times 10^{14}$  and  $5 \times 10^{13}$   $\text{cm}^{-2} \text{s}^{-1}$ , respectively, substantially higher. Both facilities were utilized in this work.

#### 4. Procedure

Our work focused on the analysis of radio impurities in KamLAND liquid scintillator and its

components. The scintillator is composed of 80% dodecane ( $\text{C}_{12}\text{H}_{26}$ ) and 20% 1,2,4-trimethylbenzene (pseudocumene,  $\text{C}_9\text{H}_{12}$ ). About 1.5 g/l solid 2,5-diphenyloxazole (PPO,  $\text{C}_{15}\text{H}_{11}\text{NO}$ ), acting as the primary fluor, is dissolved in it.

##### 4.1. Sample preparation

The analyzed samples of liquid scintillator were obtained directly from the KamLAND experimental site in Japan. For sample collection and storage, one liter PFA Teflon containers were etched in sub-boiling 25% ultra-pure nitric acid and 25% ultra-pure hydrochloric acid over a period of 1 week. The containers were then rinsed with ultra-pure water (MilliQ) and dried. Liquid scintillator was accessed in a clean room surrounding the liquid plumbing of the detector. An access tap was cleaned with alcohol and water, and then 5 l of scintillator was drained through it. Scintillator was then emptied into the collection containers, shaken and discarded. A second filling with scintillator was kept for analysis. The Teflon containers were closed, heat sealed in class 100 grade nylon bags, and shipped to the analysis laboratories at Caltech and the University of Alabama in the US.

Samples required further preparation at the US laboratories prior to neutron activation. Evaporation of the liquid at low temperature and under vacuum leaves behind most of the solid PPO powder, the least volatile component. The PPO can therefore be used as a convenient collection medium for the elements of interest. Since for K, Th and U only very few volatile chemical compounds exist, we would expect that recovery for the elements of interest after evaporating the liquid should be almost quantitative.

After evaporation the PPO was heated and transferred to a small container for irradiation. A plastic nalgene bottle of 1 cm diameter and 2 cm length was used initially for this purpose; the lid was melted and fused to the bottle with a clean soldering iron. To reach lower blank levels and allow for longer irradiations, high purity, Suprasil T21 quartz vessels from Heraeus Amersil were alternatively used in later irradiations. The quartz bottle was derived from  $8 \times 10$  mm quartz tube

stock. A 10 cm length was cut from the tube and blown shut in one end. The center of the tube was then pinched inwards until a 3 mm opening remained. The bottle was etched with a regimen of concentrated acids, followed by a rinse of ultra-pure water. For PPO transfer, the quartz was heated to near 80°C to ensure efficient movement of the organic into the bottom of the bottle. On several runs, the evaporation beaker was rinsed by an additional 1 ml of liquid scintillator which was then also poured into the quartz vessel, and dried in the same apparatus. After loading the sample, the quartz vessels were sealed by melting the pinched area closed. Liquid nitrogen was applied continuously to the bottom of the bottle in order to freeze the sample, and prevent mass loss through PPO melting and boiling.<sup>1</sup>

The sample preparation and analysis strategy depends critically on the retention of the elements of interest in the PPO. Our measurements of the retention efficiency are discussed in Section 5.

#### 4.2. Irradiation and analysis

Evaporated PPO samples were then irradiated. A test run at HFIR in October 2000 verified the feasibility of the techniques described above. The data reported here derive from irradiations at MITR between January 2001 and July 2002. When encased in plastic bottles, the PPO samples were shown to survive 15 min in HFIR or 2 h in MITR before sample boiling caused plastic bottle breaches and losses. When sealed in quartz, the sample containment survived at least 28 h of irradiation in the MITR 2PH1 pneumatic facility, without evidence of loss. The neutron flux was calibrated at MITR by irradiating trace amounts of salts of sodium, potassium, chromium, zinc, bromine, strontium, tin, antimony, lanthanum, gold, thorium and uranium, all in identical quartz and plastic bottles. The calibrated neutron flux varied from 3.0 to  $4.3 \times 10^{13}$  thermal n/(cm<sup>2</sup> s) and from  $4.1$  to  $8.9 \times 10^{11}$  epithermal n/(cm<sup>2</sup> s) (neutron energies larger than 0.5 eV), with a 8% precision in the determinations.

The pneumatic tube 2PH1 is one of the highest neutron flux irradiation facilities at the MITR. This facility allows a sample to be inserted pneumatically into a heavy water reflector tank re-entrant thimble for irradiation. Once the irradiation is terminated, the sample is ejected to a hot cell that is used for temporary storage. A CO<sub>2</sub> purge is maintained in the thimble which helps to reduce the amount of <sup>41</sup>Ar produced. The sample holder (rabbit) is a polyethylene cylinder that has a 1-3/8" ID and is 6-1/4" long. Multiple PPO samples can be accommodated in one rabbit. After irradiation, samples were allowed to cool at a hot cell for at least 12 h, in order to minimize the radiation hazard of short-lived activities, such as <sup>31</sup>Si. The samples were then packed for overnight FedEx shipment to Caltech and UA. The delay between sample ejection from the reactor and receipt at the laboratories was reduced to 35 h, improving sensitivity to short-lived activities such as <sup>42</sup>K ( $T_{1/2} = 12.36$  h).

Upon receipt at the analysis laboratories, each sample was processed for radiation analysis in a fume hood. The processing involved several steps. In the first step, the exterior of each sample container, whether quartz or plastic, was cleaned, in order to remove external contamination unconnected with the sample. An initial acetone rinse removed residual organics and connected activities. Then each sample container was immersed in a small bottle containing 60 ml of concentrated nitric acid or aqua regia. After 1 h, each sample was moved to a fresh acid vessel and the process was repeated. The acetone and two acid washes were directly assayed to confirm that extractable contamination sharply dropped from one wash to the next. Studies with additional exterior washes yielded external activities significantly lower than the activity extracted from the interior of all samples, indicating that the procedure was effective. Typical external activity reductions of <sup>24</sup>Na greater than 1000 were achieved. No evidence of external uranium or thorium contamination was seen in the washes, and only trace potassium levels were seen.

After exterior washes, the sample container was rinsed by pure water, and then broken to expose its interior. The open containers were placed in

<sup>1</sup> It is advisable to perform this operation under vacuum to prevent potentially hazardous condensation of O<sub>2</sub>.

beakers to which strong nitric acid was added, in order to extract the radioactivity from the sample itself. The acid was heated to 80°C on a hot plate for over a half hour. At this temperature, the sample of irradiated PPO was fully digested by the acid, forming a transparent yellow solution. The sample container was extracted from the hot acid, and rinsed with a few drops of acid back into the beaker. The acid was allowed to cool, which typically precipitated the PPO. By decanting or centrifugation, the acid was extracted into a separate PE bottle. The process was then repeated in which a fresh batch redissolved the residual PPO sample and etched the sample container in a new beaker, to further extract adsorbed activity. All of these acid solutions were then collected and assayed.

High-purity germanium detector spectrometers at Caltech and UA were used to assay the radionuclides in the acid. Two such detectors exist at each institution for this work. Each detector is surrounded by approximately 10 cm of lead and 5 cm of copper to reduce external backgrounds. It is important to note that a low background counting facility is essential for this study because radiochemistry separation methods are employed to remove competing activities. The detector performances vary in relative NaI efficiency from 30% to 85% at 1332 keV, resolution from 2 to 5 keV, and ambient background from  $4 \times 10^{-5}$  to  $2 \times 10^{-3}$  counts/(s keV) at 300 keV.

During the acid counting, one is limited to 10 ppt sensitivity in a gram of irradiated material for activities tagging uranium and thorium. The overall spectrometer counting rate is dominated by the decay radiation of  $^{82}\text{Br}$  and  $^{24}\text{Na}$ , originating from sodium and bromine naturally abundant in the scintillator. Partial energy depositions from the Compton scattering of high energy gamma radiation typically produce backgrounds of 1.5 counts/(s keV) near 300 keV. A further radiochemical step isolates actinides from these sources of backgrounds. The acid is poured through a plastic column containing actinide absorbing resin; the TRU or Actinide resin of Eichrom Technologies, Inc. were used. To reduce the remaining PPO precipitant in the acid which may clog the column, the acid was prefiltered with either a column of

inactive resin or a disposable plastic filter. Ideally, the column selectively absorbs actinide activities while allowing sodium, bromine, and other light elements to pass through harmlessly. In practice, we noted a reduction of greater than 100 for the sodium activity, and greater than 5 for bromine, for a typical background in the  $^{233}\text{Pa}$  and  $^{239}\text{Np}$  region of interest of  $4\text{--}80 \times 10^{-3}$  counts/(s keV).

The 100 ml polyethylene bottle containing the extracted nitric acid was counted in a high-resolution germanium detector for 12 h or more, in order to detect the presence of short-lived nuclei. The acid counting focused on  $^{42}\text{K}$  detection. The column was sealed in a bag and taped to the top of a germanium detector for radiation assay; the column's small size (1 cm diameter by 5 cm length) provided for a high efficiency in gamma-ray detection. The column data provided a sensitive measure of uranium- and thorium-related activity. The detection efficiency of the germanium counters was determined using nine-activity solutions from Isotope Products Laboratories and Northern Analytics with gamma activities spanning 88–1836 keV calibrated to 3%. The calibration solution was diluted with acid and then filled into containers with identical counting geometry and liquid volume as those used in the neutron activation analysis. The detector efficiency in each geometry was determined for each calibrated activity, and a six parameter calibration function was fitted to the data. The absolute uncertainty on the germanium detectors' efficiencies from this determination is 6%. In practice, repeated measurements of the same sample showed an activity variance of 10%, where the spread results from imprecision in geometric sample placement around the detector.

As an example for the counting procedure, Figs. 1 and 2 depict the analysis of  $^{82}\text{Br}$  in activated scintillator residue. The left panel of Fig. 2 shows part of a typical gamma spectrum obtained after counting the ion exchange column. The six peaks are due to the decay of  $^{82}\text{Br}$ , one of the main interferences. The good energy resolution and large peak to Compton ratio of the Germanium counter is used to isolate the gamma lines. Partial activities displayed for every peak show that the counting efficiency correction is

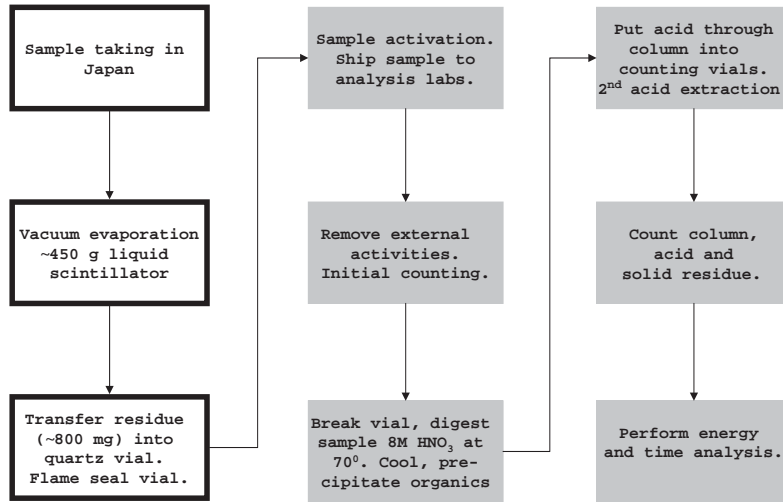


Fig. 1. Flow diagram of the principal steps involved with the described analysis. Steps displayed in a white box were performed under clean conditions to prevent introduction of contamination. Once the samples were activated no such precautions were needed. The steps involving work with relatively high activity samples are displayed in grey boxes.

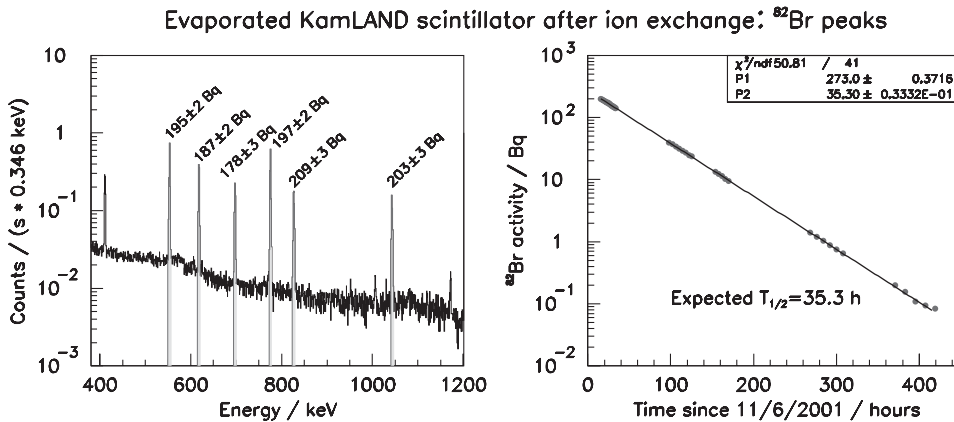


Fig. 2. Part of a typical gamma spectrum (left) and time evolution (right) of the determined activities. The parameters p1 and p2 are denoting the activity at time zero in Bq and the half life in hours, respectively.

consistent. The right panel shows the temporal development of the weighted average of all partial Br activities. A least-squares fit to an exponential decay is used to determine the activity at time zero. This double differential analysis allows for an unambiguous identification of the various radionuclides contained in the sample and offers a compact way to summarize the numerous peak integrals. For the quantitative analysis, the half life was fixed to the known value. The masses of

the elements of interest were then inferred from the measured activities using the known neutron flux and energy distribution. The equations governing this calculation are well known [5] and shall not be repeated here.

A full suite of samples for neutron activation analysis included one or more copies of a KamLAND scintillator fluid for analysis, in addition to a neutron fluence standard, one or more spiked scintillator calibration standards, an

analysis reproducibility standard, and a complementary pure water blank for each of the preceding materials. Not all of these samples were available during all irradiations. Procedures describing contamination controls are included in the Appendix A.

## 5. Determination of the efficiency

Samples of liquid scintillator quantitatively prepared with large trace element impurities monitored the overall efficiency of the analysis. Metallo-organic element standards dissolved in mineral oil were purchased from Alfa Aesar for potassium, tin, and lanthanum. For uranium and thorium, no commercial organic standard was available, so acid sources were extracted into a form soluble in organic liquids by tri-*n*-butyl phosphate (TBP) extraction [10]. For uranium, uranyl nitrate dissolved in 5 ml 1 M HCl was washed with three lots of 5 ml TBP. For thorium, thorium nitrate crystals were dissolved in a 15 ml solution of 7M  $\text{Ca}(\text{CO}_3)_2/2$  M  $\text{HNO}_3$ . This was washed with three 15 ml lots of TBP. In each case, the TBP or commercial standard was dissolved in liquid scintillator and diluted to near 10 ppb element impurity. ICPMS, NAA, and low background gamma-ray assay were all used to calibrate the final element impurities with a 10% uncertainty.

For spiked sample preparation and radiochemical analysis, completely separate but identical laboratories and equipment were used in order to avoid cross-contamination. Only the germanium detectors used for the counting were common between the calibration and clean samples. In an identical evaporator as described for the clean analysis, an approximately 1 g aliquot of standard impure scintillator was mixed with 50 ml KamLAND scintillator and evaporated. This calibration sample was collected, bottled, irradiated, radiochemically extracted and finally counted for trace activities.

Irradiation of scintillator with known element concentrations yielded information about the element transfer in the analysis process. Element concentrations in the standard spiked scintillator

Table 1

Percent recovery of uranium and thorium by radiochemical activation analysis with column extraction (an Eichrom actinide column in this case). These efficiencies calibrate the full analysis, including evaporation, irradiation, and radiochemical procedures

Method	Amount recovered in actinide column in (%)	
	$^{232}\text{Th}$	$^{238}\text{U}$
NAA	$33 \pm 23$	$67 \pm 40$

were inferred from the activities measured in the extraction acid and actinide column. The values were compared to the known impurity of the scintillator to derive an analysis efficiency for the entire process. The results are summarized in Table 1. Efficiency is clearly demonstrated for all the analyzed elements, though the efficiencies do not approach 100%.

The overall efficiency encompasses a variety of retention and loss mechanisms including element loss in evaporation and inefficient activity extraction into acid and into actinide columns. These were measured separately in order to better understand the sources of inefficiencies. The retention efficiencies are shown in Tables 2 and 3.

The chemical efficiency of the ion exchange process was calibrated separately. This determination does not need to rely on knowledge of the element concentration in the spike solution, it can be done by comparing measured activities before and after ion exchange. To do that, the analyzed activities were separated between the ion exchange column, residual acid and solid residue of irradiated sample. The sum of these three partial activities constitute 100% of induced activity. Repeated studies of the radiochemical extraction showed little change in the activity recovery with variations in certain aspects of the above procedure, including mineral acid composition, acid strength, filtration techniques, vial breaking technique, and acid digestion temperature. As an additional constraint, a straightforward separation of  $^{237}\text{Np}$  was carried out on Eichrom TRU-Spec columns. A solution of  $^{237}\text{Np}$  in 8 M nitric acid was employed as a tracer. About 15 ml of tracer solution was allowed to drain through the column

Table 2

Averaged percent recovery of elements, compared to the expected from a standard impurity, for an acid digestion of evaporated liquid scintillator samples. The scintillator evaporation is expected to dominate the losses. The errors given correspond to the standard deviation observed for repeated measurements. The number of calibration measurements performed over the course of this study is given in brackets

Method	Average amount recovered in acid in (%)				
	<sup>41</sup> K	<sup>112</sup> Sn	<sup>139</sup> La	<sup>232</sup> Th	<sup>238</sup> U
ICPMS					82 ± 17 (7)
NAA	35 ± 20 (3)	50 ± 23 (2)	52 ± 15 (3)	45 ± 34 (2)	73 ± 37 (5)

Table 3

Percent recovered activities in Eichrom TRU resin column and residual acid, after column extraction. The balance of the activities stays in the scintillator residue

Retention in	<sup>24</sup> Na(%)	<sup>42</sup> K(%)	<sup>82</sup> Br(%)	<sup>233</sup> Pa(%)	<sup>239</sup> Np(%)
Column	0.01 ± 0.01	0.1 ± 0.1	17.5 ± 1.1	96.3 ± 9.5	84.8 ± 8.1
Acid	85.1 ± 6.8	94.7 ± 12.6	60.5 ± 3.4	0.4 ± 0.3	1.2 ± 0.3

and was followed by consecutive washes of 8 M HNO<sub>3</sub>. The first acid wash of 4 ml was analyzed for <sup>237</sup>Np by liquid scintillation and was found to contain only 2.8% of the total <sup>237</sup>Np added to the column. Analysis of the elutant during loading of the <sup>237</sup>Np tracer sample showed no detectable breakthrough of the tracer. The tracer was eluted from the column with 93% recovery using a single 4 ml water wash as determined by liquid scintillation. A second column was treated in similar manner to establish blank values for the liquid scintillation detection. The reproducibility of the <sup>237</sup>Np recovery was approximately 5% for three determinations.

Activation analyses of clean scintillators are corrected for these measured efficiencies. Note that the purpose of this work is to demonstrate trace element purity of materials, rather than precisely calibrate the impurities. The precision in the determination of the analysis efficiency in the tables is sufficient for this purpose. It is noted that the full analysis efficiency for <sup>232</sup>Th and <sup>238</sup>U, as reported in Table 1 is consistent with the product of the partial efficiencies measured for the sample evaporation and column retention, given in Tables 2 and 3. The control over the element concentrations in the low-level organic spike solutions, used to derive these efficiencies, contributes to the

relatively large fluctuations observed. From the above data we conclude that trace impurity concentration can be determined quantitatively within a factor of two accuracy when applying the methods and procedures discussed in this paper.

## 6. Results

During the application of the activation analysis for KamLAND, three representative organic materials were analyzed. The impurity concentrations derived from activation analysis are shown in Table 4. Different lots of PPO from Packard BioScience were screened for purity before they were mixed with the other scintillator components. PPO 21-634 is one such lot. Since the PPO contributes only 0.2% of the final scintillator mass, it was required to be less than  $5 \times 10^{-12}$  g/g in radionuclides to reach the reactor anti-neutrino goals defined in the introduction. The PPO was directly irradiated in plastic containers, without any evaporation. During final scintillator production for KamLAND, all of the PPO lots were predissolved in pseudocumene. The concentrated PPO in PC at 200 g/l was screened prior to final scintillator mixing. The mixture was evaporated and irradiated in plastic vials.

Liquid scintillator sampled from the KamLAND detector was finally analyzed using these techniques. The 1000 tons were filled into KamLAND over a 6 months period. Samples of the scintillator fluid were taken as it entered the detector, during the second and fourth month. These samples were evaporated and irradiated in quartz. Their analysis is labeled “LS Sample #1 and #2” in the table. At the end of the filling period, a sample of final detector fluid was taken and analyzed. Each of the liquid scintillator samples was evaporated and irradiated in pure quartz vials. In the filling samples, a potassium impurity was detected, but its strength varied between the two samples studied. The final detector LS had no detectable radioimpurity.

The sensitivity to these trace radionuclides reached below  $8 \times 10^{-15}$  g/g, and the final

scintillator material was proven pure at this level. These sensitivities were sufficient to certify the organic materials as suitable for the KamLAND reactor anti-neutrino experiment.

Analysis consistency was monitored by repeatedly analyzing the same material during five irradiations. The reproducibility and laboratory to laboratory consistency was verified by repeated analysis of PPO samples of production batch 21-634. To quantify variations in our sample treatment, the effective concentrations of Na in the acid, discharged from the ion exchange column, and of Br, in the columns, was determined. The concentrations are labeled “effective” because 100% retention efficiency in the respective medium has been assumed. The retention efficiency for Na in acid has been determined to be  $(85 \pm 7)\%$ . The retention of Br in the column is estimated to be

Table 4

Impurity of KamLAND liquid scintillator materials determined with activation analysis. For null signals, 90% confidence limits on the contamination are shown

Material	Mass (g)	$^{40}\text{K}$ (g/g)	$^{232}\text{Th}$ (g/g)	$^{238}\text{U}$ (g/g)
PPO Lot 21-634	3.43	$< 8.8 \times 10^{-12}$	$(3.2 \pm 1.1) \times 10^{-12}$	$< 2.7 \times 10^{-12}$
Evap. PC + PPO	0.86	$< 73 \times 10^{-12}$	$< 1.5 \times 10^{-12}$	$< 2 \times 10^{-11}$
LS Sample #1	500.9	$(5.3 \pm 0.7) \times 10^{-13}$	$< 15.8 \times 10^{-14}$	$< 5.1 \times 10^{-14}$
LS Sample #2	96.7	$(3.1 \pm 0.6) \times 10^{-14}$	$(1.8 \pm 0.6) \times 10^{-14}$	$< 1.3 \times 10^{-14}$
KamLAND final liquid scint.	353.0	$< 2.4 \times 10^{-15}$	$< 5.5 \times 10^{-15}$	$< 8 \times 10^{-15}$

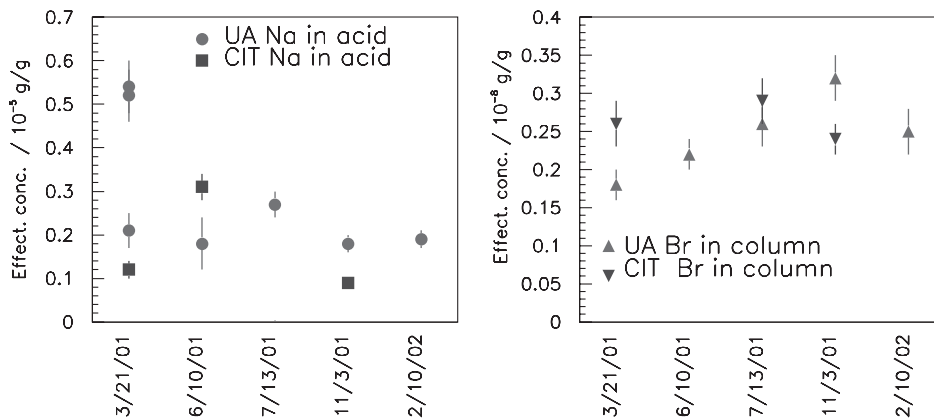


Fig. 3. Analysis consistency as determined through repeated analysis of PPO batch 21-634. The left part of the figure shows the effective concentration of Na, as determined from the acid used in radio chemical postirradiation preparation. The right part shows the effective Br concentration as determined from counting of the ion exchange columns.

about  $(18 \pm 1)\%$ . Na and Br have been chosen because they exhibit the lowest preparation blank and therefore most robust signature. Fig. 3 depicts the results of this repeated analysis. The concentrations derived for Br vary by about  $\pm 5\%$  when averaged over all activation runs. The average Br concentration derived at Caltech  $((2.56 \pm 0.15) \times 10^{-9})$  and UA  $((2.31 \pm 0.11) \times 10^{-9})$  agree within  $1.4 \sigma$ .

## 7. Conclusion

The primordial activities potassium-40, thorium and uranium constitute important sources of background for low-energy, low-rate experiments. Access to sensitive detection techniques is crucial in the development of next generation neutrino oscillation, double beta decay and dark matter experiments. The analysis technique described in this article might also be important for the development of a next generation ultra-low background counting facility in the planned US National Underground Science Laboratory.

In this paper, we discuss a novel ultra-sensitive neutron activation analysis, optimized towards the detection of primordial activities in liquid scintillator. The achieved sensitivity is below  $8 \times 10^{-15}$  g/g. The described procedure is applicable at almost any research reactor facility.

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## Appendix A

A key concern in high sensitivity analysis is the control of contamination during the analysis. A number of details regarding the measures taken in this work to control contaminations are included here. In order to address the level of potential contaminations in sample extraction, similar containers, both empty and half full with ultrapure water, were exposed to the air at the liquid access point for 1 week. The containers were filled with hot, concentrated nitric acid for 1 day, and the acid was then analyzed by ICPMS. No uranium or thorium contamination was detected. A limit of  $< 9 \times 10^{-16}$  g/l of fluid maximum contamination from the above collection process was inferred, when properly extrapolated to the collection conditions.

Contamination control during evaporation is another challenge of the technique. After evaporation of 600 ml of liquid scintillator, the typical sample size of about 800 mg results in a much higher vulnerability towards the introduction of contaminations. The cleanliness requirements during sample evaporation and handling are thus very stringent.

Scintillator evaporation at low temperatures takes very long thus resulting in a prolonged exposure to contamination. It was observed that significant loss of PPO occurs if the scintillator is evaporated at higher temperatures. Vacuum evaporation offered the best compromise between evaporation speed and PPO retention. Evaporation of scintillator samples at various temperatures showed that at temperatures between  $63^\circ\text{C}$  and  $75^\circ\text{C}$ , 70% of the PPO is recovered while the evaporation rate of about 2 g/h is still reasonable. The evaporation rate scales approximately linearly with the temperature and reaches 20 g/h at  $95^\circ\text{C}$ . All sample evaporations were performed in the above temperature range and at a pressure of about 40 torr.

- (1) All work was done in class 100 or 500 clean rooms, to avoid sample contamination.
- (2) The evaporations were performed using Sheldon Model 1415 vacuum ovens.
- (3) During evaporation vacuum was maintained using an oil-free Teflon diaphragm pump.

In order to provide an overall monitor of contamination during the sample preparation, empty quartz or plastic vessels were irradiated in parallel with samples. The procedure for evaporating the scintillator involves transferring the liquid between several PFA vessels until the PPO residue reaches the irradiation bottle, so that one is particularly sensitive to contamination during this sample handling. This contamination was monitored in practice by duplicating the procedures with ultra-pure water. Water certified to purity of  $<5 \times 10^{-12}$  g/g potassium and  $<5 \times 10^{-15}$  g/g uranium and thorium was purchased from Tama Chemicals, and was evaporated in parallel to scintillator samples, using the same equipment. At the temperature and pressure used for scintillator evaporation, the water completely evaporates in a few hours. After opening the oven to recover the PPO beaker, 1 ml of fresh water was added to the blank evaporation beakers and was poured into quartz irradiation containers. These were evaporated to dryness in the same oven and sealed. The resulting containers were then irradiated and analyzed in parallel with the samples,

using all the same steps and techniques described in the text.

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