

Measurement of trace ^{129}I concentrations in CsI powder and organic liquid scintillator with accelerator mass spectrometry

K.J. Dong ^{a,b}, M. He ^a, S. Jiang ^a, H.T. Wong ^{b,*}, J.Z. Qiu ^{a,c}, Y.J. Guan ^a, S.H. Li ^a, S.Y. Wu ^a, M. Lin ^a, Q.B. You ^a, Y.W. Bao ^a, Y.M. Hu ^a, D. Zhou ^a, X.Y. Yin ^a, J. Yuan ^a

^a Department of Nuclear Physics, Institute of Atomic Energy, Beijing 102413, China

^b Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

^c Armed Police Force Academy, Langfang 065000, China

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Abstract

Levels of trace radiopurity in active detector materials is a subject of major concern in low-background experiments. Procedures were devised to measure trace concentrations of ^{129}I in the inorganic salt CsI as well as in organic liquid scintillator with Accelerator Mass Spectrometry (AMS). Improvements in sensitivities by several orders of magnitude over other methods were achieved. No evidence of ^{129}I contaminations in CsI and liquid scintillator were observed, from which limits of $<1.5 \times 10^{-13}$ g/g and $<2.6 \times 10^{-17}$ g/g, respectively, were derived. These are the first results in a research program whose goals are to develop techniques to measure trace radioactivity in detector materials by AMS.

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1. Introduction

Measurement of trace concentrations of naturally-occurring, as well as cosmic-ray or fission induced radioactive isotopes is an important technique with major impact to low-background experiments, such as those for Dark Matter searches, as well as the studies of double beta decays, reactor and solar neutrinos [1]. The TEXONO Collaboration is pursuing a research program in low-energy neutrino and astroparticle physics [2]. One of the frontiers is to devise procedures for measuring such trace radiopurity using the techniques of Accelerator Mass Spectrometry (AMS) [3,4], with which significant improvements in sensitivities and flexibilities over existing methods can be expected. In this article, we reported on the measurement of trace ^{129}I in inorganic crystal and organic liquid scintil-

lators with the AMS facility at the China Institute of Atomic Energy (CIAE) [5], shown schematically in Fig. 1.

The isotope ^{129}I is a long-lived (half-life 1.57×10^7 years) fission product with yields of 0.74% and 1.5% from thermal neutron-induced fissions of ^{235}U and ^{239}Pu , respectively. It is commonly found in the environment, iodine being readily soluble in water. Measurements of trace ^{129}I concentration are adopted world-wide for nuclear safeguards, through the detection and prevention of accidental or deliberate discharge of nuclear waste debris into the environment [6]. Another application is on radioactive dating of, for instance, oil field materials [7].

The isotope ^{129}I decays via

$$^{129}\text{I} \rightarrow ^{129}\text{Xe}^* + e^- \quad (\tau_{1/2} = 1.57 \times 10^7 \text{ y}; Q_{\beta} = 194 \text{ keV}),$$

$$^{129}\text{Xe}^* \rightarrow ^{129}\text{Xe} + \gamma \quad (\tau_{1/2} = 0.97 \text{ ns}; E_{\gamma} = 39.6 \text{ keV}).$$

Such processes can contribute to the background in Dark Matter [1,8] and low-energy neutrino experiments, such

* Corresponding author. Tel.: +886 2 2789 6789; fax: +886 2 2788 9828.
E-mail address: htwong@phys.sinica.edu.tw (H.T. Wong).

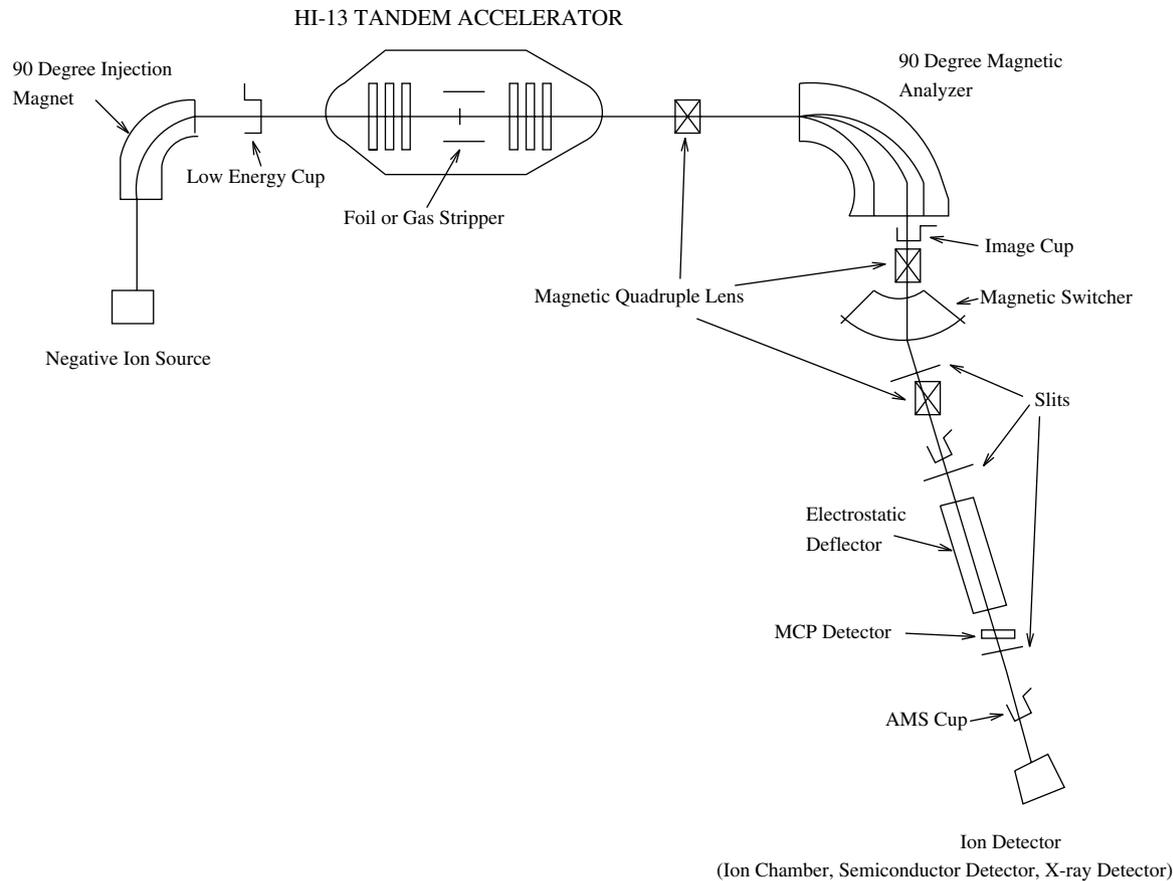


Fig. 1. Schematic layout of the 13 MV tandem accelerator facility at CIAE for AMS.

as the searches of neutrino magnetic moments [1,9]. Concentrations of ^{129}I can also indicate the contamination levels of other problematic fission fragments such as ^{137}Cs inherently present in the materials.

The techniques of measuring ^{129}I with AMS are by now matured, following early works in the 1980s [10]. They improve over the various other measurement methods with Radio-chemical Neutron Activation Analysis [11], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [12] and Liquid Scintillation Counting [13]. The AMS technique has strong rejection capabilities for isobaric, molecular and isotopic interferences, providing powerful background suppression. It is therefore widely considered as the best among the various measurement methods, where sensitivities would exceed the others' by three-to-four orders of magnitudes. The technique is commonly adopted for environmental monitoring. For instance, anomalous concentrations of ^{129}I in rainwater samples collected shortly after the Chernobyl accident were measured by AMS [14].

Measurement of trace radiopurity in detector materials is a subject of great importance in low-background experiments. It is usually performed by high-purity germanium detectors [15] or, in the most elaborate case, with dedicated big-volume liquid scintillator [16]. Both of these techniques are not applicable to ^{129}I . We extended the list of measurable isotopes to include ^{129}I by the AMS methods.

An organic liquid and an inorganic salt were selected for studies since they require different experimental procedures and systematic effect considerations. The organic liquid studied is the standard mesitylene(1,3,5-trimethylbenzene) + PPO liquid scintillator (LS) mixture.¹ The processing and measurement procedures with other organic solvent and dyes are expected to be very similar. The inorganic salt selected was CsI powder², since CsI(Tl) crystal scintillators are being used in reactor neutrino [17] and dark matter [18] experiments. Being iodine based, the ^{129}I contaminations are expected to be higher compared to the other materials.

2. Experimental set-up and procedures

In a typical AMS facility, the samples to be measured are ionized by a Cs sputtering negative ion source. The ^{129}I and ^{127}I ions are selected and accelerated alternatively. The ^{129}I ions are eventually detected by a detector, while the ^{127}I current is measured by a Faraday cup.

The overall transmission efficiency common to both isotopes from the ion source to the detector is about 1%. This

¹ Supplier: Gaonengkedi Science and Technology Co. Ltd., China.

² Supplier: Chemtall GMBH, Germany.

was determined with a silver iodide (AgI) sample by comparing the currents between the “Low Energy Cup” and “AMS Cup” at the initial and final stages, respectively, as depicted in Fig. 1.

We report on the experimental details in the following sub-sections.

2.1. Pre-processing

No chemical procedures are necessary for the CsI powder which was directly used in the AMS measurement. However, CsI is a hygroscopic material which can easily lead to injector magnet excursion. Accordingly, the CsI samples were deposited quickly on to a cathode of electrolytic copper in a dry box. The cathode was then baked in an oven at 100 °C for two days prior to the measurement.

For the organic LS, an extraction procedure for the possible iodine contaminations has to be devised. There are three possible forms where iodine may exist in the LS: iodide I^- , iodate IO_3^- and organic iodine. The sample preparation procedures were adopted from previous work [19,20] and are shown schematically in Fig. 2.

A volume of 100 ml of LS was evaporated under vacuum. The residuals left behind consisted mostly of the solid PPO powder, as well as trace concentrations of the other impurities. A KI carrier solution of mass 10 mg and a solution mixed with 2 mol/l NaOH and 2 mol/l KOH in a 3:2 ratio were added to the residual solid. After stirring to ensure a homogeneous solution, the mixture was transferred into a crucible and put onto a sand bath to dry.

The dried sample was ashed into a muffle furnace at 600 °C, and then leached with de-ionized water. After being processed by a centrifuge, the iodate in the leached solutions was reduced to iodide with sulfuric acid and sodium hydrogen sulfite ($NaHSO_3$). The iodide was oxidized to iodine by the addition of sodium nitrite and then extracted with carbon tetrachloride (CCl_4). The iodine was back-extracted as iodide ions in de-ionized water by reduction with 5% $NaHSO_3$.

These extraction and back-extraction steps were repeated until the purple color of carbon tetrachloride disappeared. The aqueous phase was boiled for a short time to remove the residual CCl_4 . After cooling, a silver nitrate ($AgNO_3$) solution was added immediately and processed with a centrifuge. The end-product AgI was rinsed by de-ionized water, dried and collected. Finally, the AgI was mixed with Nb with a ratio of 1:2 and kept for subsequent AMS measurements.

As depicted in Fig. 2, all three forms of iodine were extracted into the AgI samples. The conversion efficiencies of iodine and iodate into iodide have been studied [19] and shown to be high (>95%) through comparisons with reference samples and with measurements using ICP-MS. The extraction efficiency of the iodide was 80%, as determined by comparing the mass ratio, after proper normalizations, between the extracted AgI to the KI initially introduced. This is consistent with the results from a previous investigation [20], where a tracer of ^{131}I in NaI was introduced to monitor the various steps in the recovery process.

2.2. Injection and accelerator

The ^{129}I concentration in the CsI powder and the LS extracted as AgI were measured with CIAE-AMS facility depicted schematically in Fig. 1. The tandem accelerator was operated at a terminal voltage of 8.0 MV. A “Multi-Cathode Source of Negative Ions by Cesium Sputtering” was used as the negative ion source. Forty samples were positioned on the target wheel at one time. The wheel could be rotated without affecting the vacuum conditions such that stable operating configurations were maintained during measurements of a group of samples.

The I^- negative ions extracted from cesium sputter source were focused by a trim einzel lens and a double focusing 90° deflecting magnet where the negative ion beams of interest were momentum selected. The ions were guided to an aperture of 2 mm diameter located at the entrance of the pre-acceleration tube, where they were accelerated up to about 120 keV kinetic energy. A carbon foil was attached at the head of accelerator. The molecular background was eliminated due to break-up of molecular ions.

After passing through the accelerator tank, ions with charged state 11^+ were selected by a 90° double focusing analyzing magnet with a mass energy product ($M \cdot E/Z^2$) at 200 to suppress the isotopic background. A high-resolution electrostatic deflector was placed at a branch beam line

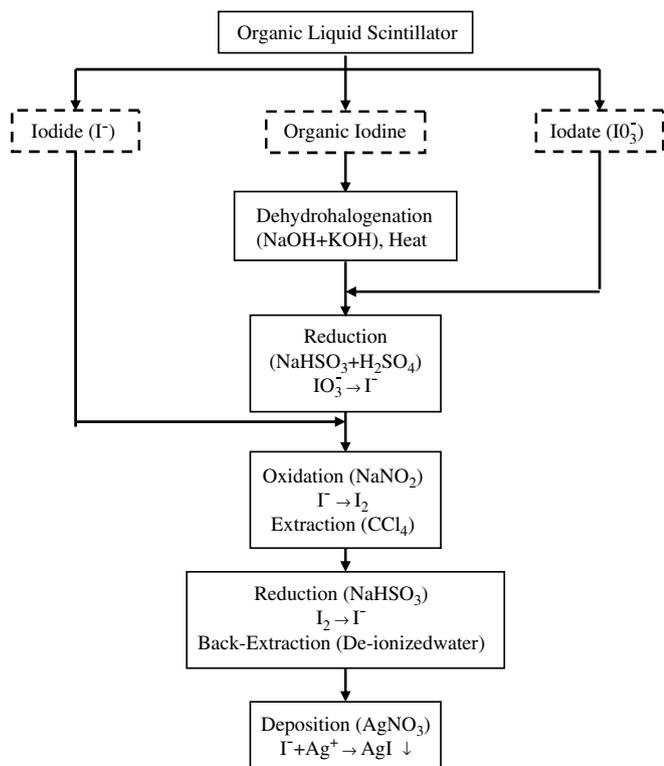


Fig. 2. The flow chart of samples preparation for organic liquid scintillator. The procedures are adopted from [19].

to further reduce the isotopic background and other undesired beam components.

2.3. Detector

Particle detection and identification of ^{129}I was performed via Time-of-Flight (TOF) detector. A detailed layout of the TOF system is shown in Fig. 3. A Micro-Channel Plate (MCP) detector provided the “START” signal while a gold-silicon surface barrier detector located 200 cm downstream was used to give a “STOP” signal. The resolution of the TOF system is 600 ps. The difference between the flight time of ^{129}I and ^{127}I was ~ 2 ns under the conditions of equal momentum at a kinetic energy of about 96 MeV.

2.4. Calibration and cross-checks

Standard AgI samples with ^{129}I were prepared and verified by the procedures described in [21].

According to the contrast results, an uncertainty better than 1% for the ^{129}I source strength in the samples could be derived. The measured $^{129}\text{I}/^{127}\text{I}$ ratios by the AMS facility were consistent to 10% with the source strength ranging from 10^{-10} to 10^{-12} .

The energy of the ^{127}I ions are 1.5% higher than that of ^{129}I ions at the same momentum. Accordingly, the ^{127}I ions would deflect more than those of ^{129}I by the electrostatic analyzer, as depicted in Fig. 4. An energy resolution ($\Delta E/E$) better than 0.5% was achieved. The TOF selection suppressed the ^{127}I by another two orders of magnitude, as shown in Fig. 5(a) for the standard sample with known concentration of $^{129}\text{I}/^{127}\text{I}$ at 1.0×10^{-10} . An “ ^{129}I -signal-box” region can be defined from this measurement to locate the ^{129}I candidate events.

2.5. Results

The suppression factors for ^{127}I due to the various AMS components are summarized in Table 1. An efficient trans-

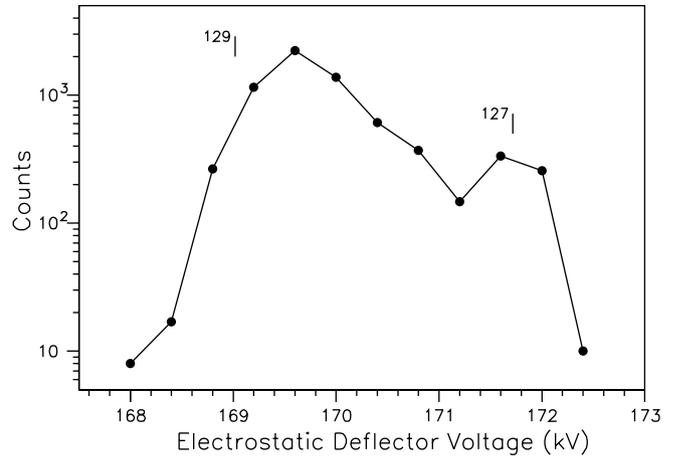


Fig. 4. The scan spectra of electrostatic deflector.

mission of ^{129}I at $\sim 60\%$ was achieved, as demonstrated by the measurements with the AgI calibration samples with known absolute strength and $^{129}\text{I}/^{127}\text{I}$ ratios.

The TOF scattered plots for the CsI and LS samples are presented in Fig. 5(b) and (c), respectively. In both of these cases, as well as in other control measurements with commercially available KI and AgI powder, the measured ^{129}I -signal-box/ ^{127}I ratios were all $\sim 3 \times 10^{-13}$. In comparison, a “blank measurement” of only the copper cathode without samples gave zero counts in the ^{129}I -signal-box, indicating that the events are iodine-related. These events can be due to actual ^{129}I contaminations in the samples as well as background from spurious effects or tail distributions of the dominant ^{127}I . Therefore, conservative limits of $^{129}\text{I}/^{127}\text{I} < 3 \times 10^{-13}$

can be derived in all four cases (CsI, LS with KI as carrier, as well as the KI and AgI control samples).

This limit is directly applicable to characterize the ^{129}I contaminations in CsI. It can be alternatively expressed as $< 1.5 \times 10^{-13}$ g/g. Accordingly, the β -decay background due to ^{129}I in CsI is less than $82 \text{ kg}^{-1} \text{ day}^{-1}$. In comparison, a recent measurement of ^{137}Cs contaminations in CsI(Tl)

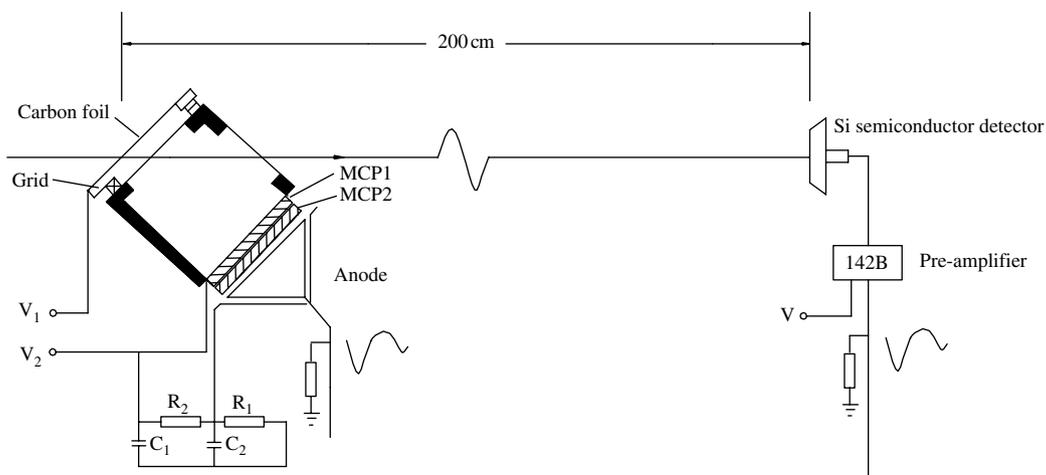


Fig. 3. The schematic layout of the time-of-flight system.

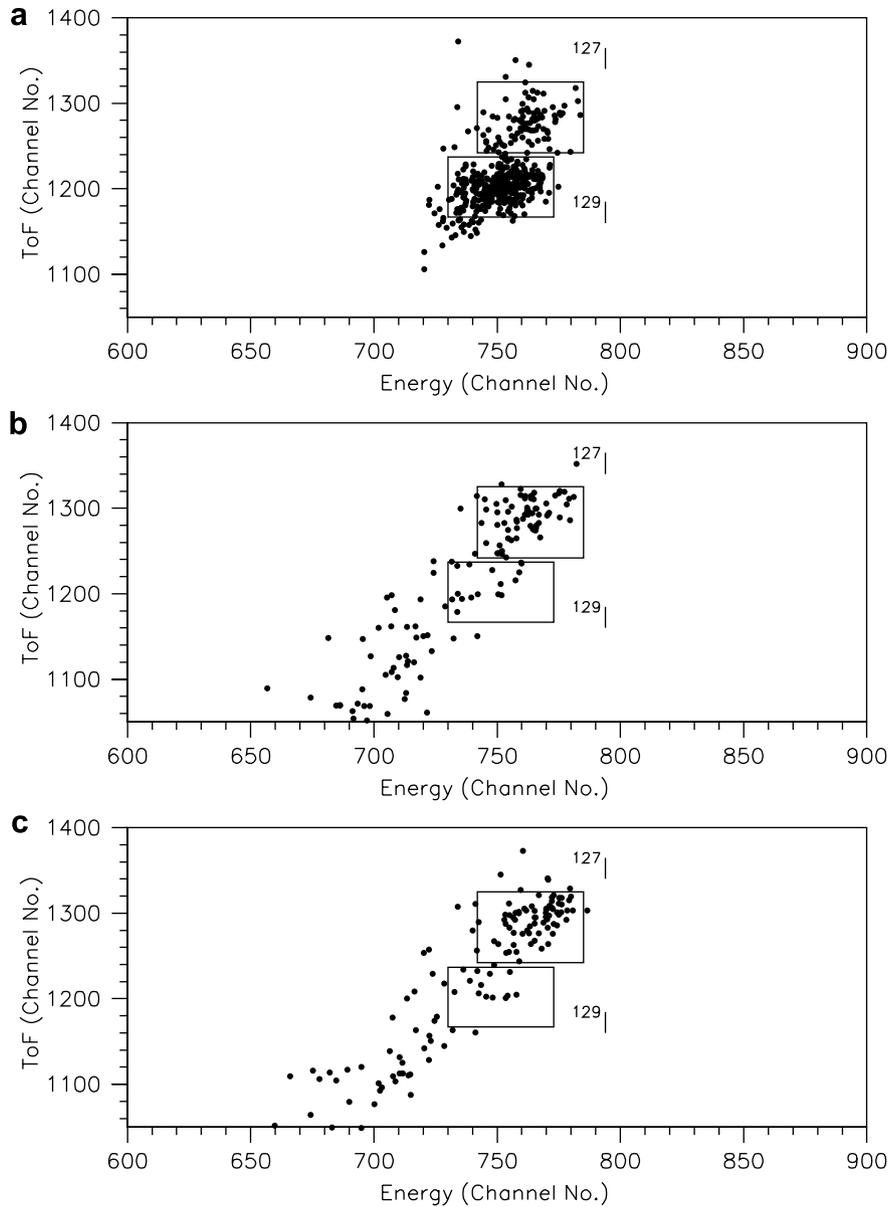


Fig. 5. TOF spectra measured by AMS on (a) reference sample at $^{129}\text{I}/^{127}\text{I} = 1.0 \times 10^{10}$, with which the ^{129}I -signal-box can be defined, (b) CsI powder and (c) liquid scintillator. There are no evidence of excess of ^{129}I above the background from ^{127}I in (b) and (c).

Table 1

Rejection power of ^{127}I and transmission efficiency of ^{129}I for the various components in the AMS facility. In addition to these factors, there is an $\sim 1\%$ overall transmission efficiency applicable to both isotopes

Components	^{127}I rejection	^{129}I transmission
Deflecting magnet	$\sim 10^{-3}$	~ 1
Analyzing magnet	$\sim 10^{-6}$	~ 1
Electrostatic deflector	$\sim 10^{-2}$	~ 0.8
TOF detector	$\sim 10^{-2}$	~ 0.8
Total	$\sim 10^{-13}$	~ 0.6

crystals [22] was $(1.55 \pm 0.05) \times 10^{-17}$ g/g. Both ^{137}Cs and ^{129}I are fission fragments found in the environment, such that their contamination levels in CsI are expected to be similar. Measurement sensitivity for ^{137}Cs by the photon-

counting technique is much enhanced due to its much shorter half-life and the emissions of mono-energetic γ -rays which are easily identified.

For the LS measurement, the volume of the LS and the mass of the KI carrier were known, from which the limit of ^{129}I concentration in LS of $< 2.6 \times 10^{-17}$ g/g can be derived, implying a background β -decay rate in LS of less than $15 \text{ ton}^{-1} \text{ day}^{-1}$.

Further improvement on the sensitivities in the LS measurements is possible, through the use of larger initial LS samples as well as reduced KI mass in the carrier solution. In addition, if the residual events in the ^{129}I -signal-box can be identified to be background from ^{127}I through more detailed studies of the TOF system response, the limits can also be improved.

3. Conclusion

Measurements on the ^{129}I concentrations in an inorganic salt and organic liquid scintillator were performed with the AMS techniques. No evidence were observed for ^{129}I contaminations and sensitive limits were derived. The limits are relevant to the design and interpretation of various low-background experiments.

The measurements of ^{129}I are the first “demonstration-of-principle” efforts of devising techniques and procedures in the trace radiopurity measurements of naturally-occurring isotopes using AMS. Research program on the applications of AMS techniques to ^{40}K and ^{87}Rb are being pursued, while those for heavier isotopes like ^{238}U and ^{232}Th series are being planned.

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