Inhibition of $^{137}$Cs contamination in cesium iodide


$^a$Department of Physics, Sejong University, Seoul 143-747, Republic of Korea
$^b$Department of Science Education, Ewha Woman’s University, Seoul 120-750, Republic of Korea
$^c$Physics Department, Yonsei University, Seoul 120-749, Republic of Korea
$^d$Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100039, China
$^e$Physics Department, Kyungpook National University, Daegu, 702-701, Republic of Korea
$^f$School of Physics and DMRC, Seoul National University, Seoul 151-742, Republic of Korea
$^g$Special Metals Division, Chemetall GmbH, Innerstetal 2, D-38685 Langelsheim, Germany
$^h$Department of Engineering Physics, Tsinghua University, Beijing, 100084, China

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Abstract

We have extensively studied the mechanism of the $^{137}$Cs and $^{134}$Cs contamination in CsI compounds. The nuclei $^{137}$Cs and $^{134}$Cs in various samples have been studied using a HPGe detector at deep underground. The main source of the $^{137}$Cs contamination in CsI powder was water dissolved $^{137}$Cs used in the chemical process of cesium extraction at company side. We also found that $^{134}$Cs was produced mainly from $^{133}$Cs by neutron capture. We have successfully produced CsI powder containing no more than 2 mBq/kg of $^{137}$Cs by using only ultra-pure water for whole extraction process from raw ore (pollucite).

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1. Introduction

Scintillation crystals are commonly used to search for extremely rare events of Weakly Interacting Massive Particles (WIMPs) [1] or
neutrino interactions [2]; NaI(Tl) [1], CaF$_2$(Eu) [3], CdWO$_4$ [4] are some examples. A thallium-doped cesium iodide crystal, CsI(Tl), is another interesting scintillator, since it has a high scintillation efficiency and relatively good pulse shape discrimination capability [5–9]. To use a CsI crystal in ultra low background experiments, however, it is essential to make sure that the potentially severe internal background of the crystal, specially from $^{137}$Cs and $^{134}$Cs, is low. The KIMS group has been preparing a WIMP search experiment using CsI crystals and explored the background reduction of CsI crystals [10,11].

The main internal backgrounds in CsI crystal were found to be due to the cesium and rubidium radioisotopes, $^{137}$Cs, $^{134}$Cs, and $^{87}$Rb [12]. In this report, we will concentrate only on $^{137}$Cs and $^{134}$Cs radioisotopes. The nucleus $^{137}$Cs ($t_{1/2} = 30.07$ yr, $Q = 1175.6$ keV) is a beta-emitter decaying with a 95% branching ratio to the meta-stable state ($t_{1/2} = 2.55$ min) of $^{137}$Ba at 661.7 keV. The expected background spectra for a 10cm × 10cm × 30 cm CsI(Tl) detector show that there are about 0.35 cpd (1 cpd = 1 counts/keV kg day) from 1 mBq/kg of $^{137}$Cs and 100 mBq/kg of $^{134}$Cs in the energy region, $E < 10$ keV, if a Compton suppressor surrounds the detector [9].

Almost all of the present $^{137}$Cs nuclei on earth have been produced artificially by the nuclear bomb tests, nuclear reactor accidents, and fuel reprocessing. The isotope has spread globally through air and water circulation. For example, the specific soil activity of $^{137}$Cs in the northern hemisphere, e.g. Canada, was 38 Bq/kg from a measurement performed in 1994 [13]. Surface sea water is typically contaminated at the level of a few mBq/l [14]. There are very few measurements on the contamination level of $^{137}$Cs and $^{134}$Cs in CsI crystal (or powder). The TEXONO [2] group reported $^{137}$Cs contamination in a CsI(Tl) crystal less than $4 \times 10^{-18}$ g/g (12.8 mBq/kg) using a high-purity Germanium (HPGe) detector.

We have previously studied commercially available CsI powders [12]. In this paper, we report a systematic study on the presence of cesium radioisotopes in CsI compounds and how we reduced the $^{137}$Cs contamination to a few mBq/kg level for the first time. The present study on $^{137}$Cs contamination of CsI could be applied for the other cesium compounds as well.

2. Mechanism of $^{137}$Cs and $^{134}$Cs contamination

2.1. Extraction processes of cesium from pollucite

Cesium is extracted from the pollucite ore, which is in the form of $\text{Cs}_2\text{Al}_2\text{Si}_4\text{O}_{12}(\text{H}_2\text{O})$. A typical elemental composition of Canadian pollucite from Tanco, Canada, is O (36.7%), Cs (30%), Si (22%), Al (8.5%), Na (1.3%), Rb (0.7%), H (0.2%), Li (0.2%), and K (0.1%). First the ore from Tanco as well as Bikita, Zimbabwe, is ground to fine powder at the mine site and delivered to chemical companies for the extraction of cesium. Fig. 1 shows the extraction processes of the cesium from pollucite in one of major companies producing cesium, Chemetall GmbH, Special Metals Division in Germany [16]. High purity CsI powder is 99.9999% [17]. One notes that the extraction process needs about 701 of water in the various stages to produce 1 kg of CsI powder [17].

2.2. Underground measurements

We have measured the $^{137}$Cs and $^{134}$Cs contamination levels in various samples by directly measuring the 661.7, 604.7, and 795.8 keV gamma rays with HPGe detectors. The HPGe detector (Ortec GEM100-S) was a 100% efficient, low-background co-axial detector, and it was installed in a laboratory 750 m underground in South Korea Yangyang Laboratory (Y2L). Shielding includes a 10 cm thick oxygen-free high-conductivity (OFHC) copper, and a 15 cm thick lead with the inner 10 cm composed of low-background Boliden lead. At present, there is a gap of about 10 cm between the HPGe crystal and the inner copper shield in order to house a large volume of samples. The whole detection system, including liquid nitrogen cryogenics, bottle was encapsulated, within an acrylic box to protect against radon activities. Nitrogen gas from a liquid nitrogen tank flows continuously at a level of 4 l/h inside the acrylic box. ORTEC PC-based ADC card was used for data acquisition.
The background count rate in the 660 keV region was 3 counts/(keV day). The detector has been continuously operated for more than 2 years.

2.3. Expected contents of $^{137}\text{Cs}$ from spontaneous fission

We have previously measured several CsI powders from various companies [12]. The amount of $^{137}\text{Cs}$ in commercial CsI powder ranges from 30 mBq/kg to several hundred mBq/kg. Since cesium is extracted from pollucite ore, we first studied the amount of $^{137}\text{Cs}$ in pollucite powder. The pollucite powder contained in a Marinelli beaker of 1 l (about 1.4 kg) was measured directly with a HPGe detector. Since pollucite contains 1.0–1.6% K$_2$O, a relatively high amount of potassium, the background level is too high to be sensitive to the gammas from $^{137}\text{Cs}$ and $^{134}\text{Cs}$. In a previous measurement with a HPGe detector surrounded with a Compton suppressor of NaI(Tl) crystals, we gave an upper limit of 5.8 mBq/kg for $^{137}\text{Cs}$ at the 90% confidence level [12]. Therefore, we concluded that $^{137}\text{Cs}$ in CsI crystals was mainly contaminated during chemical extraction.

Fig. 1. Extraction processes and water supplying system at Chemetall GmbH in Langelsheim, Germany. For A, we used 50% of “processing” water and 50% of “pure” water, and used only “pure” water for B. For C, we used only “ultrapure” water.
The measurement of pollucite shows the amount of U, Th nuclei as listed in Table 1. Since the half-life of $^{137}\text{Cs}$ is much shorter than these primordial nuclei, the activity of $^{137}\text{Cs}$ will be in secular equilibrium, and the expected activities of $^{137}\text{Cs}$ in 1 kg of CsI powder can be calculated as

$$A_i^{(137\text{Cs})} = \frac{A_i F_i Y_i^{(137\text{Cs})}}{2 \alpha M (\text{kg})}. \quad (1)$$

Here, $A_i$ is the activity, $F_i$ is the fission fraction, and $Y_i^{(137\text{Cs})}$ is the yield of $^{137}\text{Cs}$ in each U, Th nuclei. $\alpha$ is the relative amount of cesium in pollucite, and $M$ is the mass of the pollucite sample in kg unit.

The expected amount of $^{137}\text{Cs}$ from spontaneous fissions of U nuclei in the pollucite powder is estimated to be less than 0.1 µBq/kg as shown in Table 1, which is negligible compared to the amount present in typical CsI powder. The contributions from spontaneous fissions of $^{235}\text{U}$ and $^{232}\text{Th}$ are much smaller than for $^{238}\text{U}$ due to smaller fission fractions of these nuclei. Therefore, spontaneous fission is not the main source of $^{137}\text{Cs}$ in CsI crystals, and not a problem even when we consider a highly sensitive WIMP signal search experiment.

### 2.4. Water samples

Naturally environmental anthropogenic $^{137}\text{Cs}$ should be the source of $^{137}\text{Cs}$ in CsI powder. There are many studies on $^{137}\text{Cs}$ and $^{134}\text{Cs}$ levels in environmental water before and after the Chernobyl accident [14,15]. The average level of $^{137}\text{Cs}$ in Pacific and Indian Ocean surface water was 1–3 mBq/l [14] in the year 2000. The $^{137}\text{Cs}$ level of Finland rivers was 100–1000 mBq/l just after the Chernobyl accident, and decreased to 10–100 mBq/l in the year 1996 depending on the location of the river [15]. At present, no information on the level of $^{137}\text{Cs}$ in river water used by the company is available. Since 70 liters of water is used in the chemical process of 1 kg CsI powder production, even an extremely small amount of $^{137}\text{Cs}$ in the water could be responsible for the whole $^{137}\text{Cs}$ in commercial CsI powder.

To understand the contamination mechanism of $^{137}\text{Cs}$ and find out how to reduce the $^{137}\text{Cs}$ in CsI compounds, we have asked the company to produce CsI powder with different water supplied, as shown in Fig. 1. In the normal production procedure, mixed water from “processing” and “pure” water was supplied with the ratio of 1:1 (A). Secondary, CsI powder was produced with only “pure” water for the whole processes (B). Thirdly, high-quality ion exchangers (cartridge polisher)\(^2\) was installed after the usual ion exchanger, and only “ultrapure” water from the cartridge polisher was supplied (C). The three kinds of water, “processing”, “pure”, and “ultrapure” water were supplied from the company to us in the amount of 20 l each for analysis. In addition to the water samples, we prepared two more water samples of “ultrapure” water (18 MΩ) in the amount of 100 l produced in Korean laboratories.

To measure the extremely small activity of $^{137}\text{Cs}$ in the water samples, we used the standard method of applying AMP (Ammonium Molybdo-phosphate) to precipitate the cesium ions in the water. The water samples were supplied in polyethylene (PE) bottles, and the precipitation was

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>$T_{1/2}$ (yr)</th>
<th>$F_i$ (%)</th>
<th>$Y_i^{(137\text{Cs})}$ (%)</th>
<th>$A_i$ (Bq/kg)</th>
<th>$A_i^{(137\text{Cs})}$ (µBq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U}$</td>
<td>$4.47 \times 10^9$</td>
<td>$5.45 \times 10^{-7}$</td>
<td>0.058</td>
<td>1.93</td>
<td>0.073</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>$7.04 \times 10^8$</td>
<td>$7.0 \times 10^{-11}$</td>
<td>$\approx 0.06$</td>
<td>0.086</td>
<td>$4.32 \times 10^{-7}$</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>$1.41 \times 10^{10}$</td>
<td>$1.8 \times 10^{-11}$</td>
<td>$\approx 0.06$</td>
<td>0.24</td>
<td>$3.09 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

\(^2\)Two cartridges were installed, and the volume of each was 100 l. The throughput maximum was 2000 hl for each. The resin was a mixed bed of 40% cation exchanger and 60% anion exchanger, a product from Rohm & Haas, Amberlite MB20.
done in the same bottle. First, we added 0.5 cc of 
HNO₃ (70%) per one liter of water to the water 
container. Then we stirred the water container for 
about 10 min, and let the water stabilize several 
hours. Then we added 0.5 g of AMP per one liter 
of water to the container, and stirred the whole 
container for about 30 min. After leaving the 
container over night, the water was decanted 
slowly, and the remaining yellow liquids were 
moved to a one-liter beaker. The beaker was left 
for one day, and the upper water was decanted 
again. The remaining liquids were moved to a PE 
bottle (φ = 5 cm). We dried the PE bottle in a drier 
at about 80°C. After complete drying, the PE bottles 
were moved to the HPGe detector for measure-
ment. The detection efficiencies were simulated 
with GEANT3. All the samples were treated in the 
same way.

3. Results and discussions

3.1. ¹³⁷Cs

Fig. 2 shows the measured spectra of the three 
water samples in the energy region of ¹³⁷Cs γs. 
One of the “processing” water samples (a) shows 
clearly large ¹³⁷Cs activity, and the “pure” water 
(b) shows very little.

The three powders, A, B and C were produced 
as described in previous section (see also Fig. 1) in

a large quantity of several hundred kgs with 
different water. The powder samples were mea-
sured in a Marinelli beaker of 11, which contains 
2.9 kg of CsI powder. Fig. 3 shows the 
¹³⁷Cs contamination in measured spectra of pow-
der samples. The peak around 665 keV are due to 
the gammas from ¹³²Cs and ¹²⁶I produced by high-
energy neutrons during the transportation by 
airplane. However, these isotopes have halflives 
of 6.479 and 13.11 days, respectively, and disap-
pear after a month or so.

Table 2 lists the measured specific activities 
of ¹³⁷Cs and ¹³⁴Cs in the water and powder 
samples. The activities were 0.50–1.66 and 
0.061–0.084 mBq/l for the “processing” and 
“pure” water samples, respectively. The “ultrapure” water did not show a peak, so only an upper 
limit is obtained, 0.036 mBq/l. As shown in the 
Table 2, ¹³⁷Cs contamination is reduced by an 
order of magnitude from the best “normal” 
powder by supplying purer water.

The measured ¹³⁷Cs in the powder produced 
with “ultrapure” water only (C) was 1.89 ± 0.5 
mBq/kg, which is close to the expected upper limit 
of ¹³⁷Cs contamination from the water only. Fig. 4 
shows the expected ¹³⁷Cs activities in CsI powders

![Fig. 2. Measured spectra of water samples with HPGe detector for ¹³⁷Cs: (a) “Processing” water, (b) “pure” water, and (c) “ultrapure” water samples from Chemetall GmbH.](image1)

![Fig. 3. Measured spectra of three CsI powder samples.](image2)
Table 2
Measurements of $^{137}$Cs and $^{134}$Cs in water and CsI powder samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Description</th>
<th>$^{137}$Cs (mBq/kg)</th>
<th>$^{134}$Cs (mBq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water &quot;processing&quot; 1</td>
<td>1.66 ± 0.08</td>
<td>&lt;0.07</td>
<td></td>
</tr>
<tr>
<td>water &quot;processing&quot; 2</td>
<td>0.50 ± 0.07</td>
<td>&lt;0.06</td>
<td></td>
</tr>
<tr>
<td>water &quot;pure&quot; 1</td>
<td>0.084 ± 0.031</td>
<td>&lt;0.011</td>
<td></td>
</tr>
<tr>
<td>water &quot;pure&quot; 2</td>
<td>0.061 ± 0.018</td>
<td>&lt;0.053</td>
<td></td>
</tr>
<tr>
<td>water &quot;ultrapure&quot;</td>
<td>&lt;0.006</td>
<td>&lt;0.012</td>
<td></td>
</tr>
<tr>
<td>powder &quot;processing&quot; + &quot;pure&quot;</td>
<td>20.5 ± 2.2</td>
<td>37.2 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>powder &quot;pure&quot; water only</td>
<td>7.41 ± 0.7</td>
<td>15.9 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>powder &quot;ultrapure&quot; water only</td>
<td>1.89 ± 0.5</td>
<td>30.1 ± 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Expected activities in CsI powders from water measurements and measured activities in CsI powders. For A, we used 50% of "processing" water and 50% of "pure" water, and used only "pure" water for B. For C, we used only "ultrapure" water.

The spectra of all water samples measured did not positively show peaks from $^{134}$Cs decay. The upper limits of $^{134}$Cs in the water samples were a few tens of mBq/kg, which can contribute only a few mBq/kg in CsI powder at most. The $^{134}$Cs level in CsI powder was 16–37 mBq/kg, and there was no correlation with water quality as expected. The $^{134}$Cs in CsI powder should have been present in pollucite before cesium extraction or produced in situ in CsI powder by the neutron capture process of $^{133}$Cs. The activity of radioactive nuclei produced by constant thermal neutron flux can be written as

$$A(t) = N_0 \sigma F_n (1 - e^{-\lambda t})$$

where $N_0$ is the number of $^{133}$Cs nuclei, $\sigma$ is the Maxwell averaged capture cross section, $F_n$ is the thermal neutron flux, and $t$ is the exposure time. The thermal neutron capture cross section of $^{133}$Cs is 25.8 barn, and the typical thermal neutron flux at sea level is reported as 0.0014 neutrons cm$^{-2}$/sec [18]. With these values, we can estimate the specific activity of $^{134}$Cs to be about 49 mBq/kg for pollucite, and about 81 mBq/kg for CsI powder assuming constant flux and infinite exposure (saturation). For one year of exposure, the values are 14 and 24 mBq/kg in pollucite and CsI powders, respectively. The measured level of $^{134}$Cs in pollucite powder was 11.7 ± 3.3 mBq/kg, which is consistent with the one-year exposure value. Even if we do not know the detail history of exposure for the specific samples of pollucite and CsI, the measured activities of $^{134}$Cs in CsI powder are consistent with the production from thermal neutron capture by $^{133}$Cs during a few year exposure to environment thermal neutrons.

4. Conclusion

We have studied the contamination and inhibition of $^{137}$Cs and $^{134}$Cs in CsI powder to produce low-background CsI crystals for very low rate physics experiments such as WIMP search. The contamination of $^{137}$Cs in CsI powder and other cesium compounds was due to $^{137}$Cs in water supplied at the manufacturing sites. Using high-quality ion exchanger cartridge polisher, we could
decrease the $^{137}$Cs contamination down to 2 mBq/kg level from an otherwise a few tens of mBq/kg. The expected and measured $^{137}$Cs level in CsI powder agrees well with a few mBq/kg, and further purification can be achieved below 1 mBq/kg. At this level, there may be other sources for the contamination, such as chemicals used for the processes. We plan to study this possibilities for further purification. The $^{134}$Cs contamination level in CsI powder was 16–37 mBq/kg, unaffected by water purity. $^{134}$Cs is found to be produced mainly by environmental (cosmic) thermal neutron capture processes.

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References

[17] Private communication with Chemetall GmbH.