Development of liquid scintillator containing zirconium complex for neutrinoless double beta decay experiment

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Neutrinoless double beta decay

\[ [T_{1/2}^{0\nu}(0^+ \rightarrow 0^+)]^{-1} = G_{0\nu}(E_0, Z) |M_{0\nu}|^2 <m_\nu>^2 \]

\[ T_{1/2} \sim a(M_t/\Delta E_B) \quad a: \text{abundance} \quad M: \text{mass} \]
\[ t: \text{meas.time} \quad \Delta E: \text{energy res.} \quad B: \text{BG rate} \]

Requirement: Low BG, Large target mass, High energy resolution
For future experiments

~tons of target will be needed for next generation detector

high energy resolution
4%@2.5MeV

F.Piquemal @v2012

http://kds.kek.jp/getFile.py/access?contribId=37&sessionId=16&resId=2&materialId=slides&confld=9151
Studied isotopes

- $^{116}\text{Cd}$ → COBRA CdWO$_4$
- $^{76}\text{Ge}$ → GERDA MAJORANA
- $^{82}\text{Se}$ → SuperNEMO LUCIFER
- $^{136}\text{Xe}$ → KamLAND-Zen EXO NEXT
- $^{100}\text{Mo}$ → ZnMoO$_4$ AMoRE
- $^{130}\text{Te}$ → CUORE
- $^{48}\text{Ca}$ → CANDLES SuperNEMO AMoRE
- $^{150}\text{Nd}$ → SNO+ SuperNEMO MTD Borexino

A dream?
Detector design for Zr in 100ton LS

- Zirconium Complex in Organic liquid Scintillator (ZICOS)

Assuming 10w.t.% solubility
Zirconium $\beta$-diketon complex

- Zirconium(IV) acetylacetonate ($\text{Zr(acac)}_4$)

**Advantage**
- good solubility (over 10w.t.%) in Anisole (PhOMe)
- Stable and cheap
- Commercial product

**Disadvantage**
- Low scintillation light yield

Molecular weight: 487.66
What’s problem : Absorption spectra of Zr(acac)₄

- Emission peak of anisole was observed around 295nm.
- Absorption peak of Zr(acac)₄ was observed around 270nm.

Scintillation light from PhOMe might be absorbed by Zr(acac)₄
Simple expectation for quenting

- Assuming to same cross section for light

\[
\text{Light yield} = L_0 \times \frac{\sigma_1 N_{\text{ppo}}}{\sigma_1 N_{\text{ppo}} + \sigma_2 N_{\text{Zr}}}
\]

\(L_0\): Light yield of anisole + PPO+POPOP

\(N_{\text{ppo}}\) and \(N_{\text{Zr}}\): No. of molecular for PPO and \(\text{Zr(acac)}_4\)

\(\sigma_1, \sigma_2\): absorbance of PPO and \(\text{Zr(acac)}_4\)
Scontillation Light yield \((^{60}\text{Co})\) with respect to concentration of \(\text{Zr(acac)}_4\)

<table>
<thead>
<tr>
<th>concentration of (\text{Zr(acac)}_4)</th>
<th>Observed channel</th>
<th>Expected channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mg</td>
<td>3850</td>
<td>3850</td>
</tr>
<tr>
<td>50 mg ((1.03\times10^{-4}))</td>
<td>3175</td>
<td>3138</td>
</tr>
<tr>
<td>100 mg ((2.05\times10^{-4}))</td>
<td>2800</td>
<td>2651</td>
</tr>
<tr>
<td>200 mg ((4.10\times10^{-4}))</td>
<td>2000</td>
<td>2018</td>
</tr>
<tr>
<td>300 mg ((6.15\times10^{-4}))</td>
<td>1600</td>
<td>1613</td>
</tr>
<tr>
<td>500 mg ((1.03\times10^{-3}))</td>
<td>900</td>
<td>1178</td>
</tr>
</tbody>
</table>

PPO 100mg : \(4.52\times10^{-4}\) mol
Improve scintillation light yield

- Move absorption peak to shorter wavelength
- How to do it?
  - substituent groups

http://www.hi-ho.ne.jp/hosomi/sotsuron

Courtesy of Prof. Yoshiyuki Kowada (Hyogo University of Education)
Absorbance peak for several substituent groups

- Measured absorbance peaks for several substituent groups
- Expected absorbance peak for several substituent groups
Zr $\beta$-diketon complex introducing substituent groups ($\beta$-keto ester complex)

$\text{Zr(CH}_3\text{COCHCOOCH(CH}_3\text{))}_4 = \text{Zr(iprac)}_4$

$\text{mw} = 711.92$

$\text{Zr(CH}_3\text{CCOCHCOOCH}_3\text{)}_4 = \text{Zr(etac)}_4$

$\text{mw} = 665.81$
Zr β-keto ester complex

Zr(iprac)$_4$+(iprac)$_{1.5}$
state: powder

Zr(etac)$_4$
state: dry solid

Synthesized by Prof. Takahiro Gunji (Tokyo University of Science)

Solubility > 10 w.t.% for anisole
Absorbance spectra (Solvent effect)

Solution: Hexane

Solution: acetonitrile

Absorption peak moved to shorter wavelength
Absorbance in another solvent

Solution: Diethyl Ether

- Solvent effect could depend on the polarity (dielectric const.)
  - Acetonitrile: 37.5
  - Hexane: 1.89
  - Anisole: 4.3
- Need solution which has same polarity as anisole
  - Diethyl ether: 4.33

Still absorption peak remains around 270nm
Light yield of scintillation

Zr(iprac)$_{5.5}$ in anisole

Zr(etac)$_{4}$ in anisole

Same quenching as Zr(acac)$_{4}$ was observed
Requirement of scintillator solvent

- Low polarity (dielectric const.)
  - No absorption ~270nm
- Aromatic compounds
  - Luminescence >270nm
- Safety for human body and environment
- Usual solvent for L.S.

Toluene / Xylene
Zirconium complex with luminescence

- **Zr-ODZ complex**

\[
\text{C}_6\text{H}_5\ \text{O} = \text{N} = \text{N} = \text{O} \quad \text{Zr}^{4+} \quad 4
\]

\[
m.w. = 1040.18
\]

- **Photo luminescence**

- Solvent: Acetonitrile
- Concentration: \(3.0 \times 10^{-5}\) mol/L
Emission and absorption of $\text{Zr(ODZ)}_4$

- Emission wavelength: 430nm
  - PMT sensitive
- Absorption wavelength: 270nm and 320nm different from excitation W.L.
- Solvent: PhCN (Benzonitrile)
- Solubility: $\sim$5w.t.%
Response for $\gamma$-irradiation

- Most of emission light from PhCN was not used for the emission of Zr(ODZ)$_4$.
- Secondary excitation of $\sim$340nm was used for the emission of Zr(ODZ)$_4$.
- Estimated Quantum yield was obtained $\sim$30% at first excitation of $\sim$240nm.

Need another solvent which has shorter emission wavelength than PhCN.
Summary

- High solubility of Zr β-keto ester in Anisole (>~10w.t.% for ZICOS detector was achieved.

- Confirmed absorption peak moves to shorter wavelength (275nm → 245nm) by introducing substituent groups.

- Observed scintillation light yield decreased in proportion to the concentration of Zr β-keto ester due to remaining absorption @ 280nm. Need low polarity solvent.

- Quantum yield of Zr(ODZ)₄ was achieved ~30%, but it was not used for scintillator due to no overlap between emission of solvent and absorption of ODZ.
Neutrinoless double beta decay using liquid scintillator

- Experimental limits for neutrino mass

- Requirement for $<m_\nu>$: 50~100 meV
  - high energy resolution 4%@2.5 MeV
  - low background rate 0.01 count kg$^{-1}$ y$^{-1}$
  - ton scale of target

Liq. Scintillator is easy to scale up target volume
What’s problem

- Absorption spectra of In(acac)$_3$ (indium acetyl acetone) was overlapped with the emission spectra from Anisole (Chem. Phys. Lett., 435(2007), 252)

Same overlap of the emission and the absorption spectrum would be occurred even if different metal (Zr) was used.
Scintillation light yield ($^{137}$Cs) with respect to concentration of Zr(acac)$_4$.

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<tr>
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<td>2450</td>
<td>2450</td>
</tr>
<tr>
<td>50mg</td>
<td>1800</td>
<td>1997</td>
</tr>
<tr>
<td>100mg</td>
<td>1400</td>
<td>1687</td>
</tr>
<tr>
<td>200mg</td>
<td>950</td>
<td>1284</td>
</tr>
<tr>
<td>300mg</td>
<td>650</td>
<td>1038</td>
</tr>
<tr>
<td>500mg</td>
<td>300</td>
<td>750</td>
</tr>
</tbody>
</table>

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Photo Luminescence and absorption of PPO

- Photo luminescence
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device: HITACHI U-3000
  - Solvent: Benzonitrile (PhCN)
  - Concentration: \(1.0 \times 10^{-5}\) mol/L

- 2,5-Diphenyloxazole
  - Molecular mass: 221.26
  - Max. emission wavelength: 368.0nm
  - Max. absorption wavelength: 309.7nm
Photo Luminescence and absorption of POPOP

- Photo luminescence
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device: HITACHI U-3000
  - Solvent: Benzonitrile (PhCN)
  - Concentration: $1.0 \times 10^{-5}$ mol/L

- 1,4-Bis(5-phenyloxazol-2-yl)benzene
  - Molecular mass: 364.40
  - Max. emission wavelength: 423.6nm
  - Max. absorption wavelength: 364.1nm
Photo Luminescence and absorption of bis-MSB

- **Photo luminescence**
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device: HITACHI U-3000
  - Solvent: Benzonitrile (PhCN)
  - Concentration: $1.0 \times 10^{-5}$ mol/L

- 1,4-Bis(2-methylstyryl)benzene
  - Molecular mass: 310.44
  - Max. emission wavelength: 426.6nm
  - Max. absorption wavelength: 355.3nm
Response for $\gamma$-ray for tetrakis 8-quinolinolinate Zr complex loaded scintillator

- Tetrakis (8-quinolinolinate) Zirconium complex ($\text{ZrQ}_4$)

\[
M^{n+} \quad \text{N} \quad \text{O} \\
\text{M} = \text{In}, \text{n} = 3; \text{M} = \text{Zr}, \text{n} = 4
\]

$\text{ZrQ}_4$ m.w. = 689.07

ZrQ$_4$ 50mg in PhCN-POPOP

Quantum Yield = 1.1%

obtained by optical method

Light Yield to BC505:

$= 7.3\%$

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