

Supported by Grant-in-Aid for Scientific Research (C) 24540295 and  
Grant-in-Aid for Scientific Research on Innovative Areas 24104501

# ジルコニウム 96 を用いた二ニュート リノを放出しない 2 重ベータ崩壊事 象の探索実験 III

日本物理学会 2013年秋季大会

2013年9月20日

宮城教育大学教育学部 福田 善之

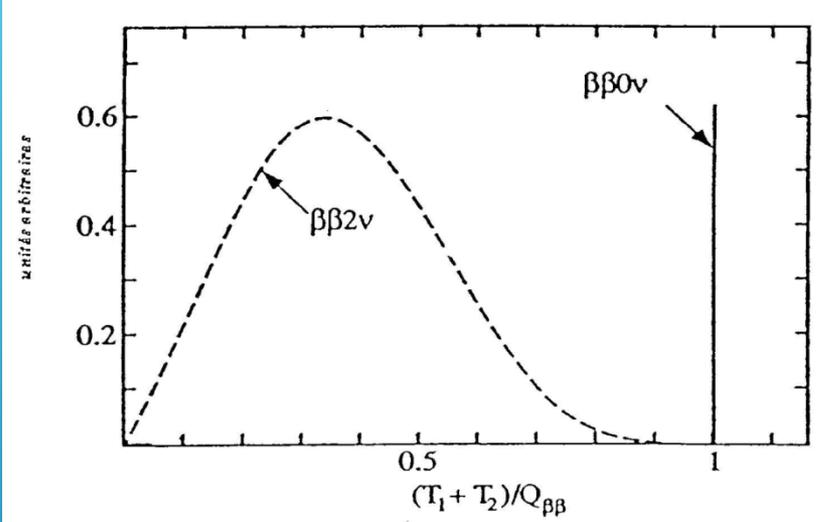
東京大学宇宙線研究所 森山 茂栄

福井大学工学部 小川 泉

# NEUTRINOLESS DOUBLE BETA DECAY

$\beta\beta$  emitters with  $Q_{\beta\beta} > 2$  Mev

Transition	$Q_{\beta\beta}$ (keV)	Abundance (%) ( $^{232}\text{Th} = 100$ )
$^{110}\text{Pd} \rightarrow ^{110}\text{Cd}$	2013	12
$^{76}\text{Ge} \rightarrow ^{76}\text{Se}$	2040	8
$^{124}\text{Sn} \rightarrow ^{124}\text{Te}$	2288	6
$^{136}\text{Xe} \rightarrow ^{136}\text{Ba}$	2479	9
$^{130}\text{Te} \rightarrow ^{130}\text{Xe}$	2533	34
$^{116}\text{Cd} \rightarrow ^{116}\text{Sn}$	2802	7
$^{82}\text{Se} \rightarrow ^{82}\text{Kr}$	2995	9
$^{100}\text{Mo} \rightarrow ^{100}\text{Ru}$	3034	10
$^{96}\text{Zr} \rightarrow ^{96}\text{Mo}$	3350	3
$^{150}\text{Nd} \rightarrow ^{150}\text{Sm}$	3667	6
$^{48}\text{Ca} \rightarrow ^{48}\text{Ti}$	4271	0.2

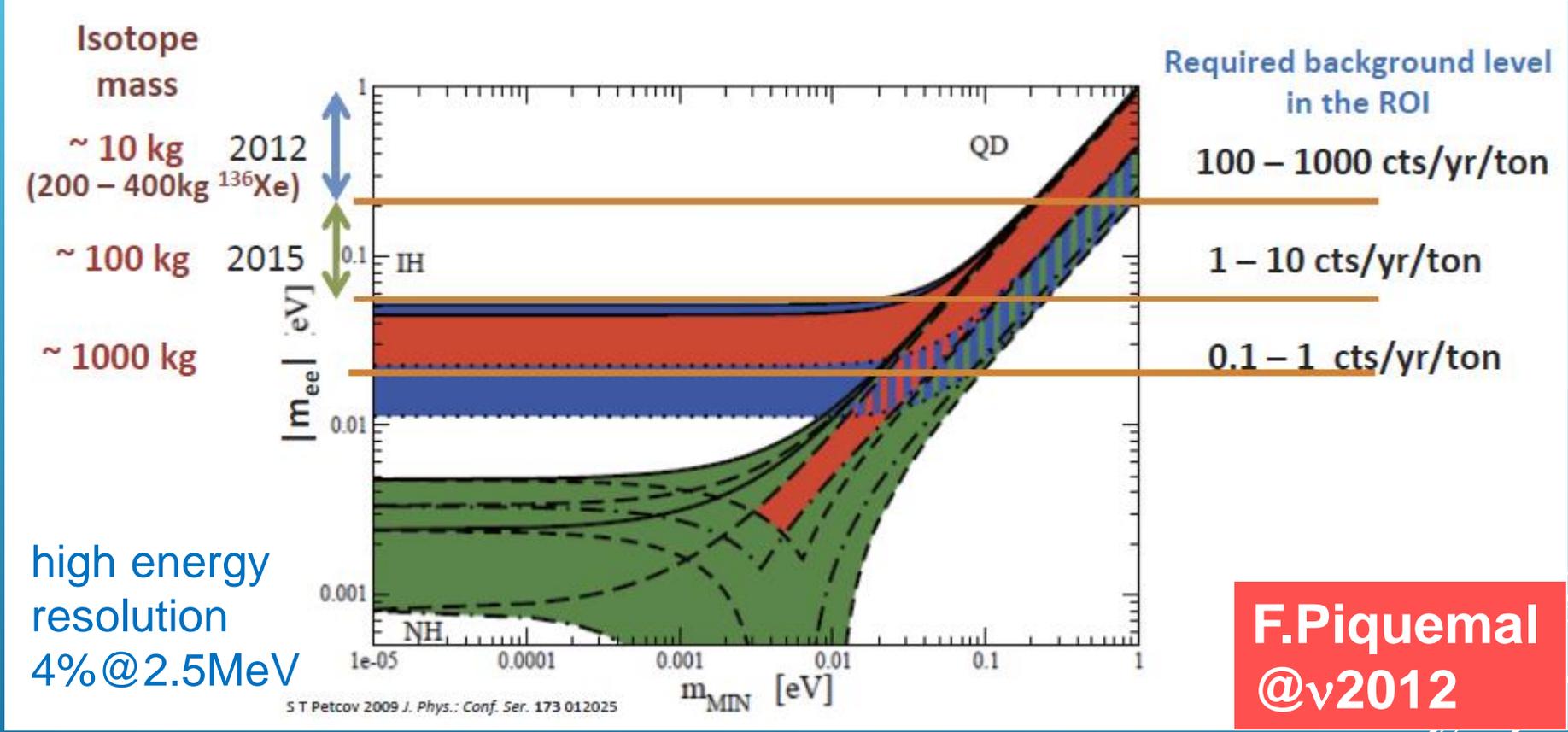


$$[T_{1/2}^{0\nu}(0^+ \rightarrow 0^+)]^{-1} = G_{0\nu}(E_0, Z) |M_{0\nu}|^2 \langle m_\nu \rangle^2$$

$T_{1/2} \sim a(Mt/\Delta EB)$        $a$ : abundance     $M$ : target mass  
 $t$ : measurement time     $\Delta E$ : energy resolution     $B$ : BG rate

**Requirement : Low BG, Large target mass, High energy resolution**

# FOR FUTURE EXPERIMENTS



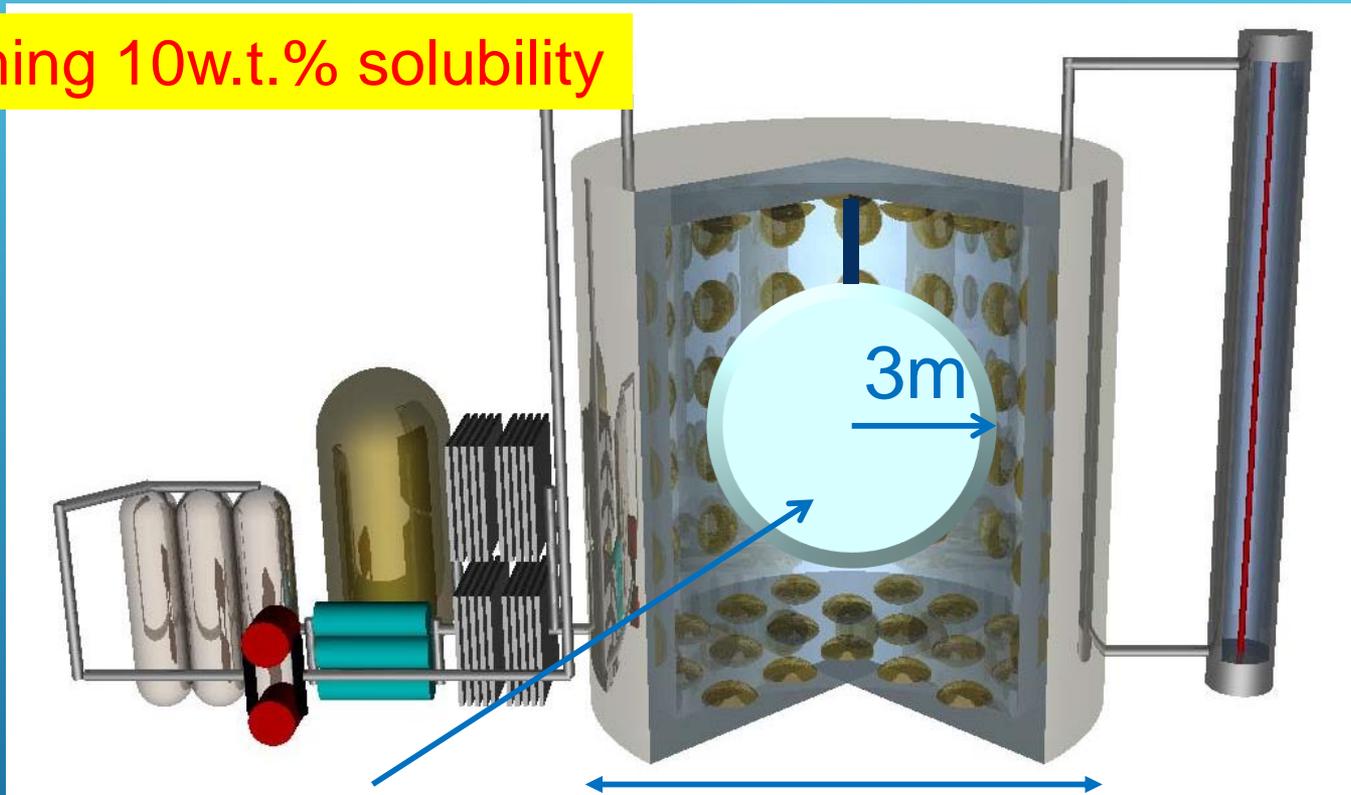
F.Piquemal  
@v2012

<http://kds.kek.jp/getFile.py/access?contribId=37&sessionId=16&resId=2&materialId=slides&confId=9151>

~tons of target will be necessary for next generation detector

# ZIRCONIUM COMPLEX IN ORGANIC LIQUID SCINTILLATOR (ZICOS) FOR DOUBLE BETA DECAY EXPERIMENT

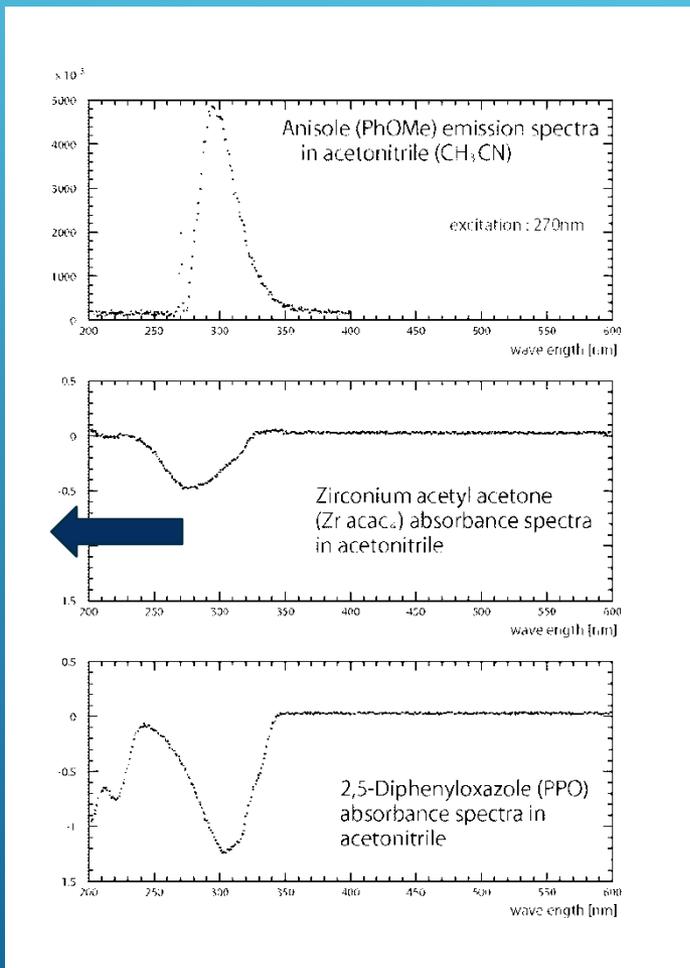
Assuming 10w.t.% solubility



Zirconium loaded 100ton LS

10m

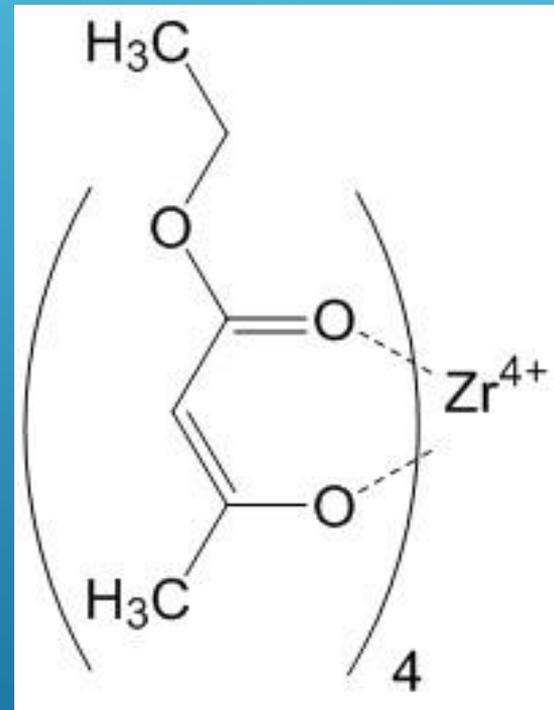
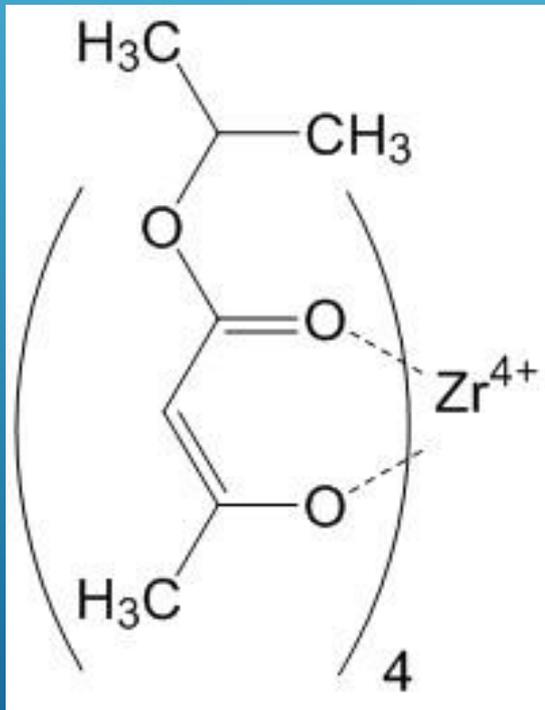
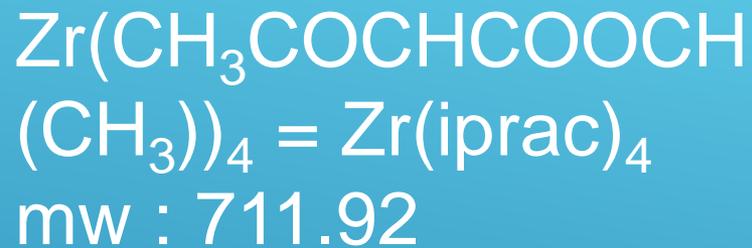
# ABSORPTION SPECTRA OF ZIRCONIUM ACETYLACETONE



- ▶ Emission peak of anisole was observed around 295nm.
- ▶ Absorption peak of Zr(acac)<sub>4</sub> was observed around 270nm.

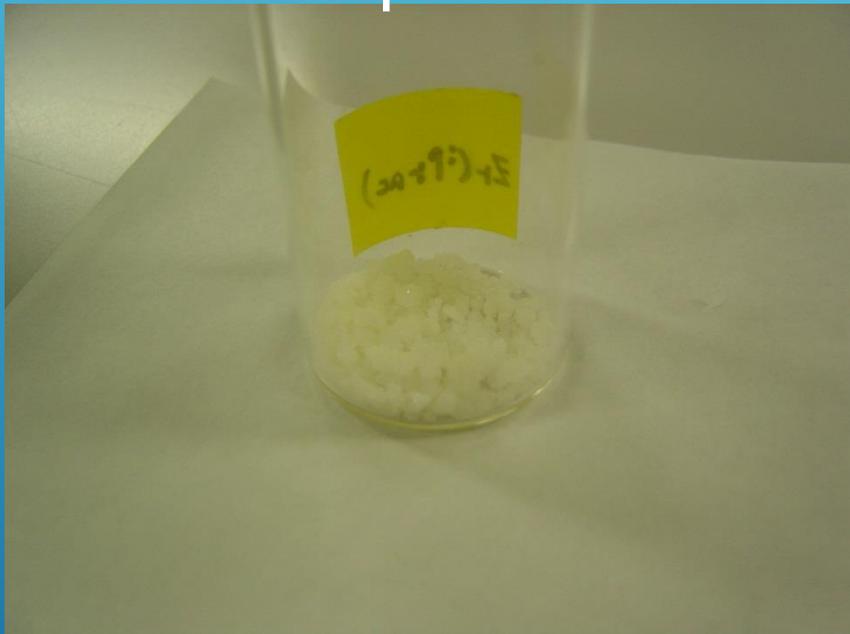
Scintillation light from anisole (PhOMe) might be absorbed by Zr(acac)<sub>4</sub>

# ZIRCONIUM BETA-KETO ESTER COMPLEX

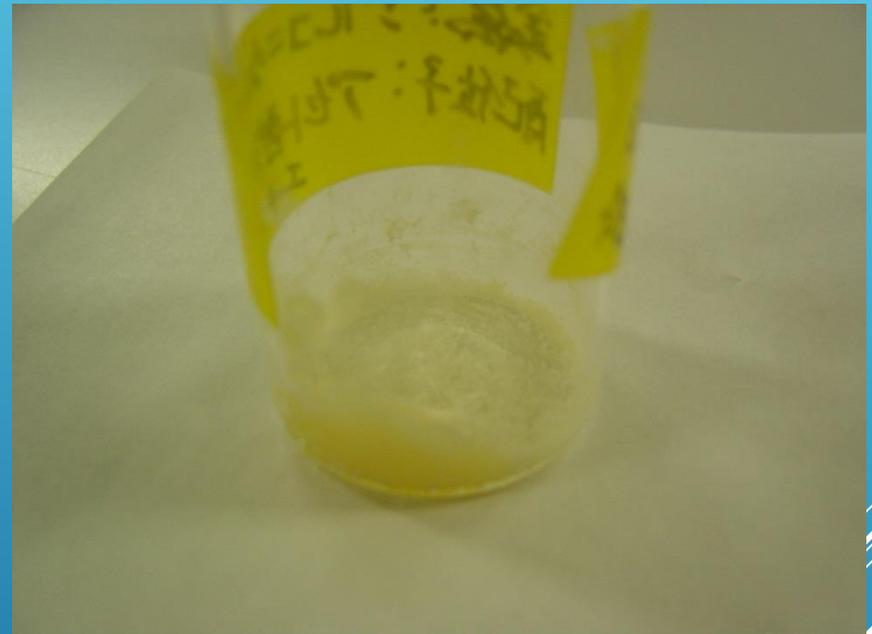


# ZIRCONIUM BETA-KETO ESTER COMPLEX

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



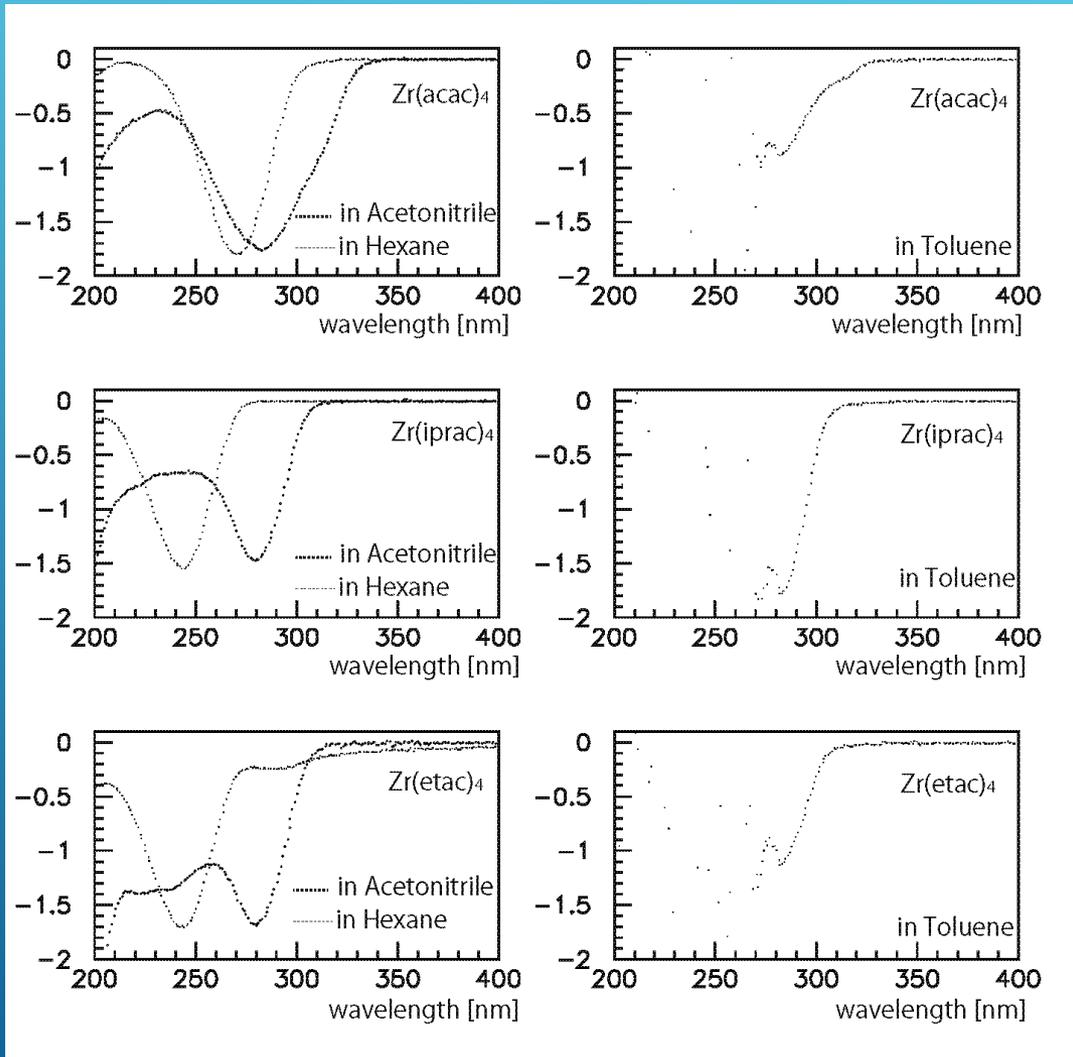
$\text{Zr(etac)}_4$   
state : dry solid



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

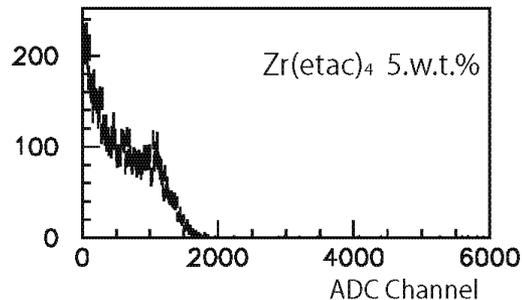
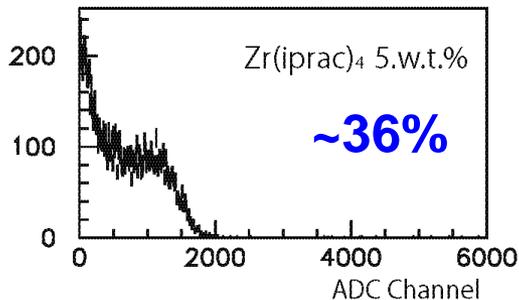
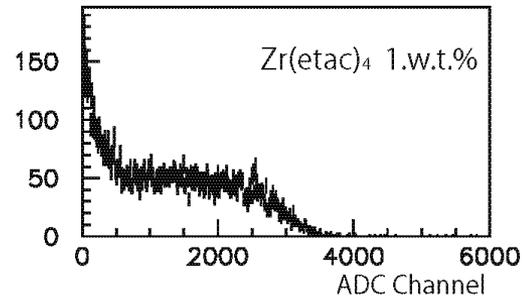
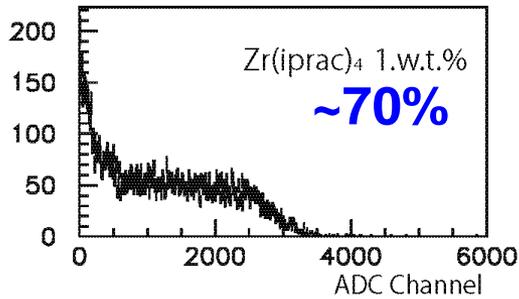
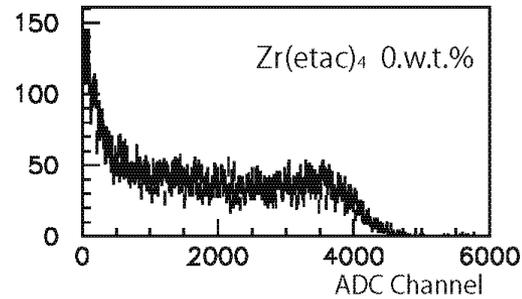
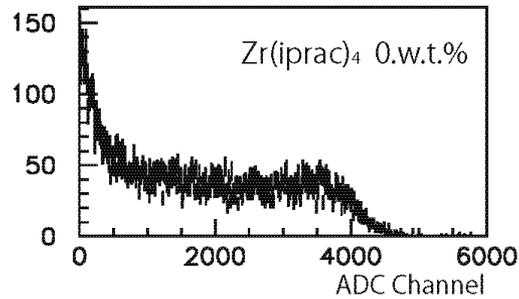
**Solubility > 10 w.t.% for anisole**

# ABSORBANCE SPECTRA FOR ZIRCONIUM BETA-KETO ESTER COMPLEX



**Confirmed the absorption peak moves 275nm → 245nm in Hexane, but in Acetonitrile (nor Toluene)**

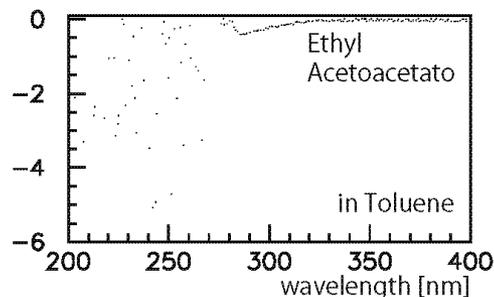
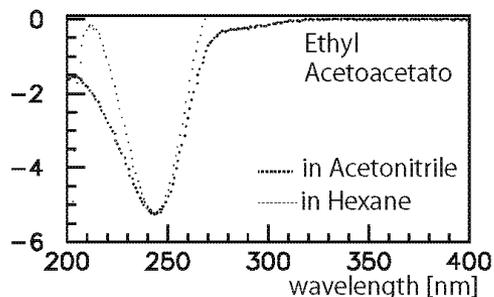
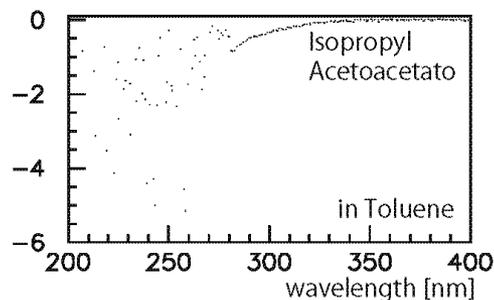
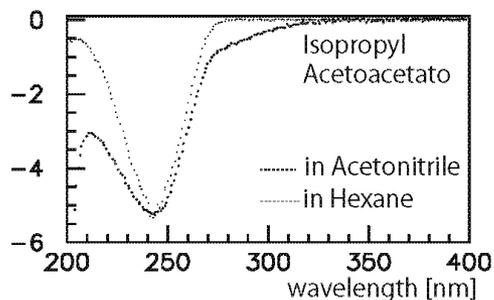
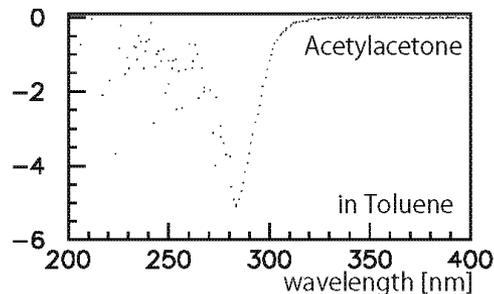
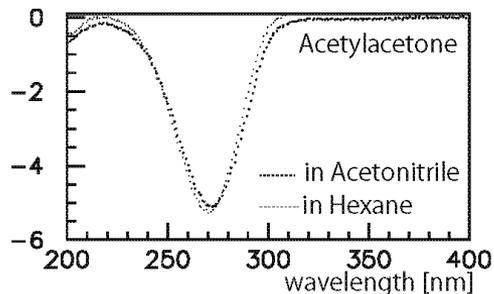
# LIGHT YIELD OF LS CONTAINING ZIRCONIUM BETA-KETO ESTER COMPLEX



**Observed  
scintillation light  
yield decreased  
due to quenching .**

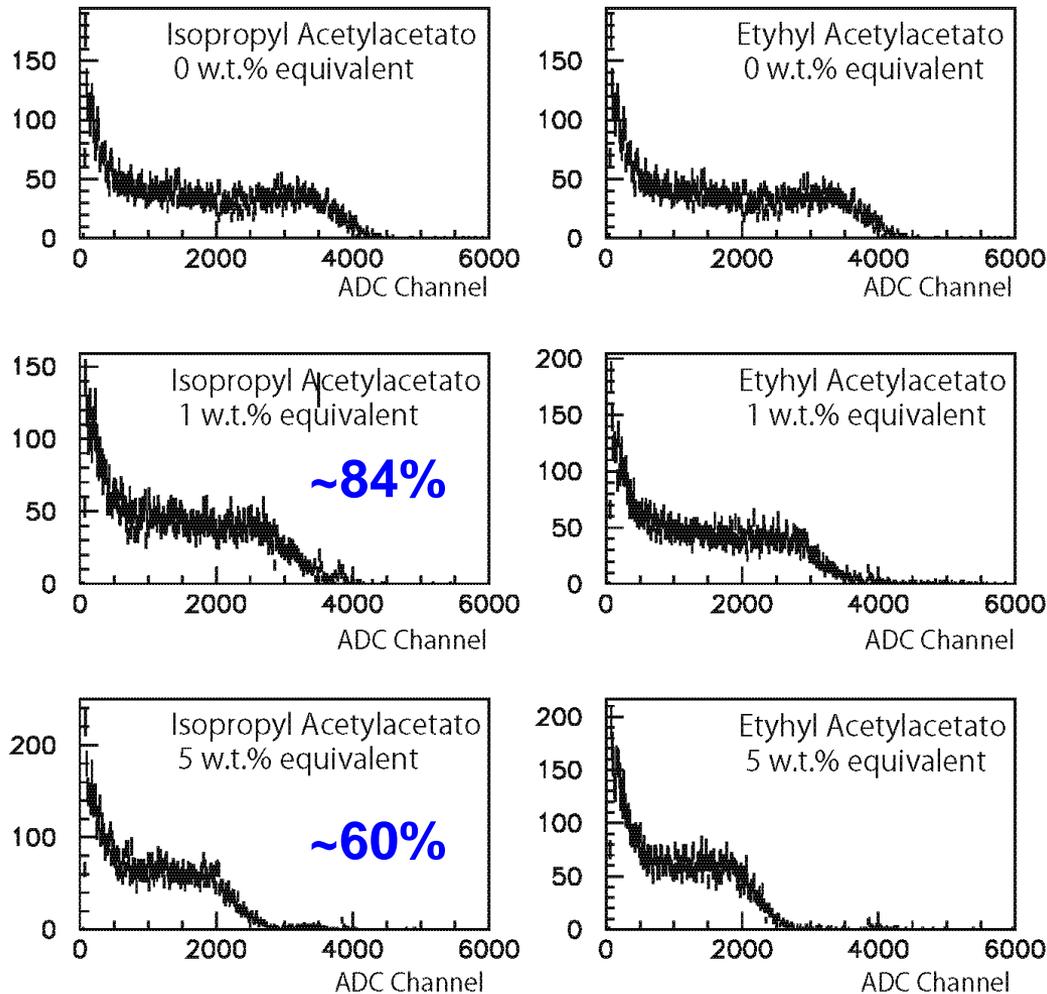
**Still exists  
absorption peak  
around 270nm in  
Anisole ?.**

# ABSORBANCE SPECTRA FOR BETA-KETO ESTER LIGAND



Absorption peaks of  $\beta$ -keto ester ligands were found around at **240nm** (not 270nm) even though the aromatic solvent.

# LIGHT YIELD OF LS CONTAINING BETA-KETO ESTER LIGAND



**Scintillation light  
yield recovers  
almost double.**

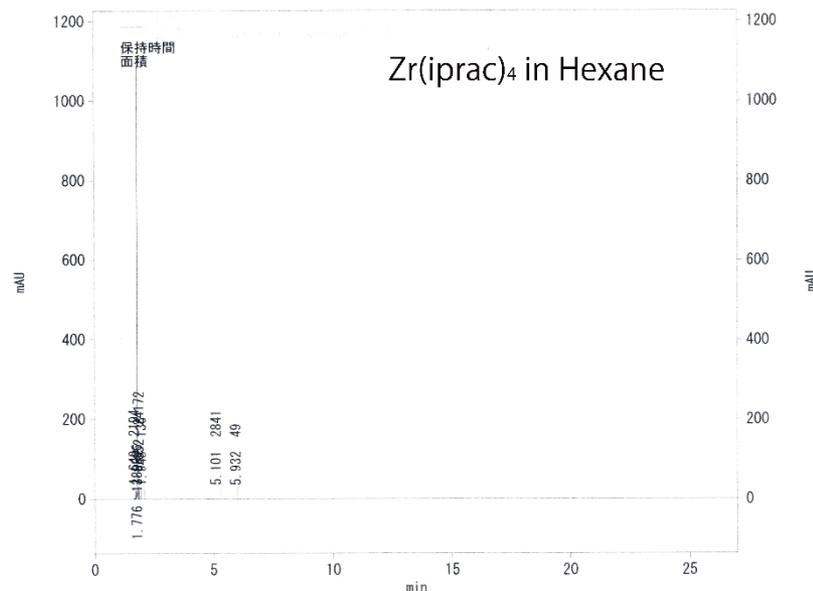
**$\beta$ -keto ester  
complex was  
dissolved in  
solvent ?**

# COMPONENT IN SOLUTION OF HEXANE

## 面積%レポート

データファイル名: C:\EZChrom  
Elite\Enterprise\Projects\Default\Data\20130913-hexane-Zr(iprac)-new-obata.dat  
メソッドファイル名: C:\EZChrom Elite\Enterprise\Projects\Default\Method\PP0\_measurement.met

分析日時: 2013/09/13 19:17:01  
印刷日時: 2013/09/13 19:44:00



FID結果 Pk #	名前	保持時間	面積	面積%	ベースラインコード*
1		1.65	2194	0.155	BV
2		1.78	1389896	97.929	VV
3		1.85	24172	1.703	VV
4		1.95	138	0.010	VB
5	hexane	5.10	2841	0.200	BB
6		5.93	49	0.003	BB
トータル			1419288	100.000	

Nothing found except Hexane.

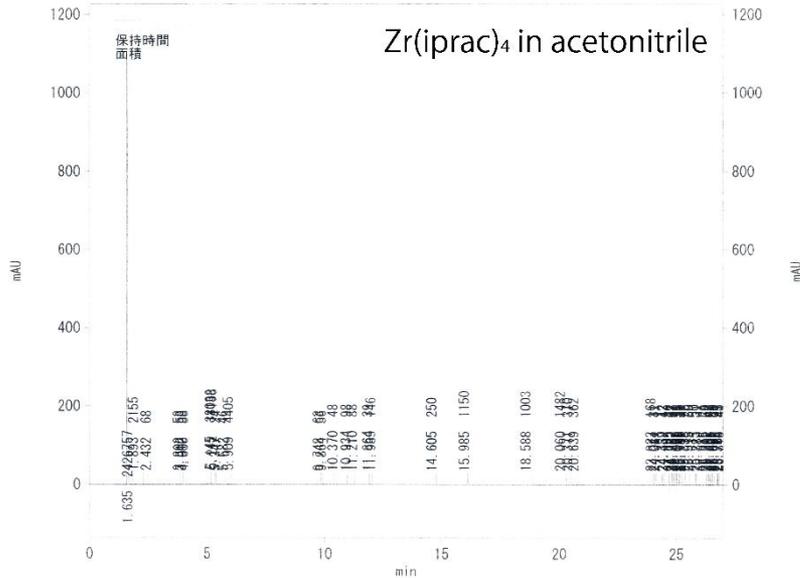
No peak of metal-complex was found in any case with GC.

# COMPONENT IN SOLUTION OF ACETONITRILE

## 面積%レポート

データファイル名: C:\EZChrom  
 Elite\Enterprise\Projects\Default\Data\20130906-acetonitril-Zr(Prac)-obata.dat  
 メソッドファイル名: C:\EZChrom Elite\Enterprise\Projects\Default\Method\PP0\_measurement.met

分析日時: 2013/09/06 13:38:51  
 印刷日時: 2013/09/06 14:05:51



FID結果	Pk #	名前	保持時間	面積	面積%	ピークコメント
	1		1.63	2426757	97.497	BV
	2	acetonitrile	1.89	2155	0.087	VB
	3		2.43	68	0.003	BB
	4		3.80	53	0.002	BB
	5		3.91	53	0.002	BV
	6		4.00	38	0.002	VB
	7		5.15	38038	1.528	BV
	8		5.21	11198	0.450	VV
	9		5.35	24	0.001	VB
	10		5.68	46	0.002	BV
	11	Isopropyl acetoacetate	5.91	4405	0.177	VB
	12		9.75	63	0.003	BV
	13		9.86	56	0.002	VB
	14		10.37	48	0.002	BB
	15		10.93	98	0.004	BB
	16		11.21	88	0.004	BB
	17		11.86	39	0.002	BB
	18		11.99	146	0.006	BB

## 面積%レポート

データファイル名: C:\EZChrom  
 Elite\Enterprise\Projects\Default\Data\20130906-acetonitril-Zr(Prac)-obata.dat  
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分析日時: 2013/09/06 13:38:51  
 印刷日時: 2013/09/06 14:05:51

19	14.60	250	0.010	BB
20	15.99	1150	0.046	BB
21	18.59	1003	0.040	BB
22	20.06	1482	0.060	BV
23	20.37	310	0.012	VV
24	20.64	362	0.015	VB
25	25.92	168	0.007	BV
26	24.04	31	0.001	VV
27	24.08	41	0.002	VB
28	24.39	12	0.000	BB
29	24.44	42	0.002	BB
30	24.70	22	0.001	BB
31	24.79	62	0.002	BV
32	24.86	32	0.001	VB
33	25.00	11	0.000	BB
34	25.03	22	0.001	BB
35	25.07	31	0.001	BV
36	25.12	17	0.001	VV
37	25.15	21	0.001	VV
38	25.19	39	0.002	VB
39	25.34	26	0.001	BB
40	25.52	30	0.001	BB
41	25.77	50	0.002	BB
42	25.88	31	0.001	BB
43	26.22	39	0.002	BV
44	26.30	59	0.002	VB
45	26.39	46	0.002	BV
46	26.49	54	0.002	VV
47	26.53	31	0.001	VV
48	26.60	50	0.002	VB
49	26.73	91	0.004	BV
50	26.76	25	0.001	VB
51	26.81	45	0.002	BB

トータル: 2489058, 100.000

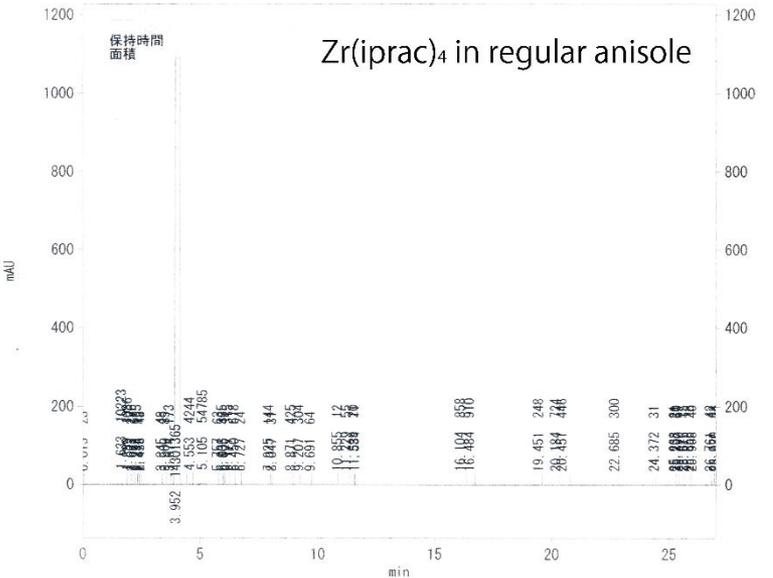
Isopropyl acetoacetate ligand was found with Acetonitrile.

Something dissolved  $\beta$ -keto ester complex.

# COMPONENT IN SOLUTION OF ANISOLE

## 面積%レポート

データファイル名: C:\EZChrom  
 Elite\Enterprise\Projects\Default\Data\20130906-anisole-Zr(Prac)-obata.dat  
 メソッドファイル名: C:\EZChrom Elite\Enterprise\Projects\Default\Method\PP0\_measurement.met  
 分析日時: 2013/09/06 15:03:58  
 印刷日時: 2013/09/06 15:30:59



FID結果 Pk #	名前	保持時間	面積	面積%	ヘキサインコード
1		0.01	23	0.000	BB
2		1.63	10223	0.071	BV
3		1.89	1086	0.008	VV
4		2.07	276	0.002	VV
5		2.22	69	0.000	VV
6		2.29	165	0.001	VV
7		2.37	75	0.001	VV
8		2.44	43	0.000	VB
9		3.35	48	0.000	BB
10		3.50	89	0.001	BV
11	anisole	3.67	173	0.001	VB
12		3.95	14301365	99.460	BB
13		4.55	4244	0.030	BB
14		5.11	54785	0.381	BB
15		5.76	63	0.000	BB
16	Isopropyl	5.93	335	0.002	BV
17	acetoacetate	6.01	49	0.000	VV
18		6.18	315	0.002	VB

## 面積%レポート

データファイル名: C:\EZChrom  
 Elite\Enterprise\Projects\Default\Data\20130906-anisole-Zr(Prac)-obata.dat  
 メソッドファイル名: C:\EZChrom Elite\Enterprise\Projects\Default\Method\PP0\_measurement.met  
 分析日時: 2013/09/06 15:03:58  
 印刷日時: 2013/09/06 15:30:59

19	6.45	678	0.005	BB
20	6.73	24	0.000	BB
21	7.92	144	0.001	BV
22	8.05	31	0.000	VB
23	8.87	425	0.003	BB
24	9.21	304	0.002	BB
25	9.69	64	0.000	BB
26	10.85	12	0.000	BB
27	11.23	55	0.000	BB
28	11.54	20	0.000	BB
29	11.58	11	0.000	BB
30	16.10	858	0.006	BB
31	16.48	910	0.006	BB
32	19.45	248	0.002	BB
33	20.18	724	0.005	BV
34	20.45	446	0.003	VB
35	22.68	300	0.002	BB
36	24.37	31	0.000	BB
37	25.24	21	0.000	VB
38	25.30	30	0.000	VB
39	25.39	69	0.000	BB
40	25.62	15	0.000	BB
41	25.86	28	0.000	BB
42	25.97	40	0.000	BB
43	26.76	42	0.000	BB
44	26.92	68	0.000	BB
45	26.99	34	0.000	BE

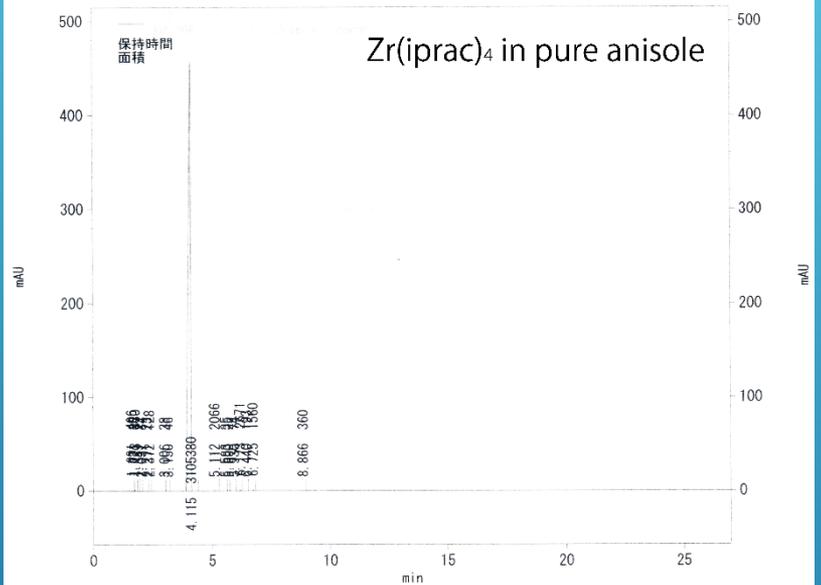
トータル 14379058 100.000

Isopropyl acetoacetate ligand was also found with Anisole.

# COMPONENT IN SOLUTION OF PURE-ANISOLE

## 面積%レポート

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 EliteEnterprise\Projects\Default\Data\20130913-anisole-Zr(iprac)-obata.dat  
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 分析日時: 2013/09/13 19:58:45  
 印刷日時: 2013/09/13 20:25:45



Nothing was found except pure anisole

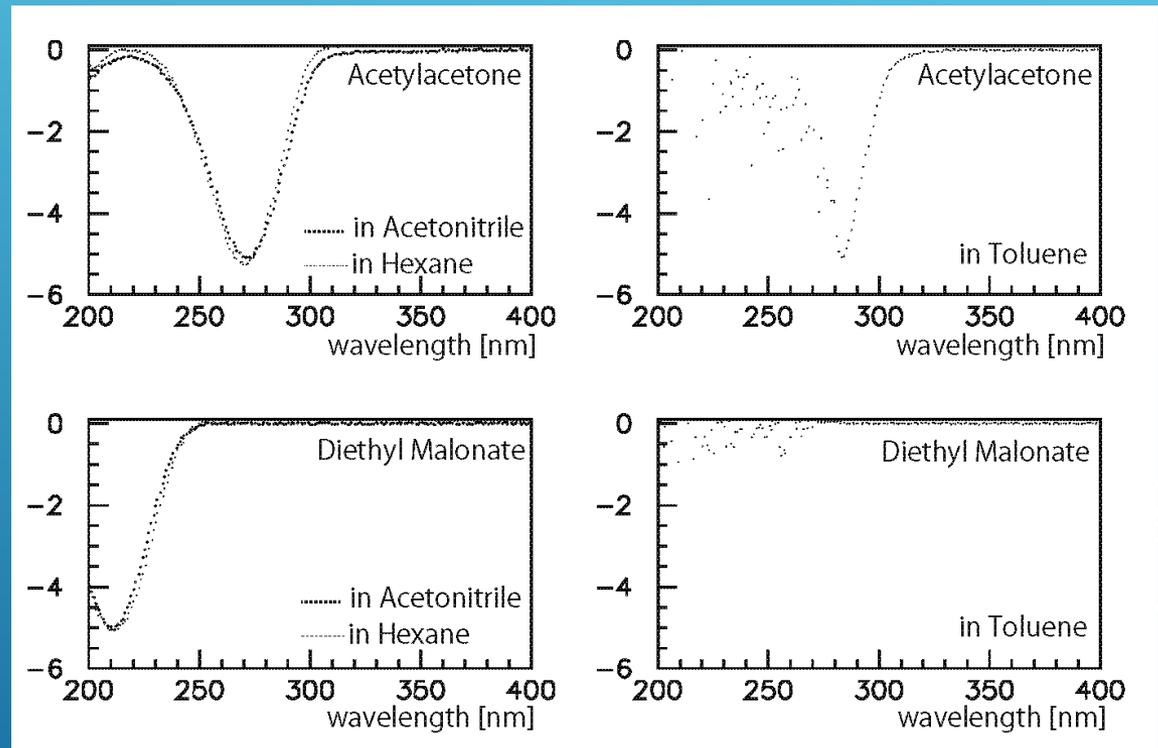
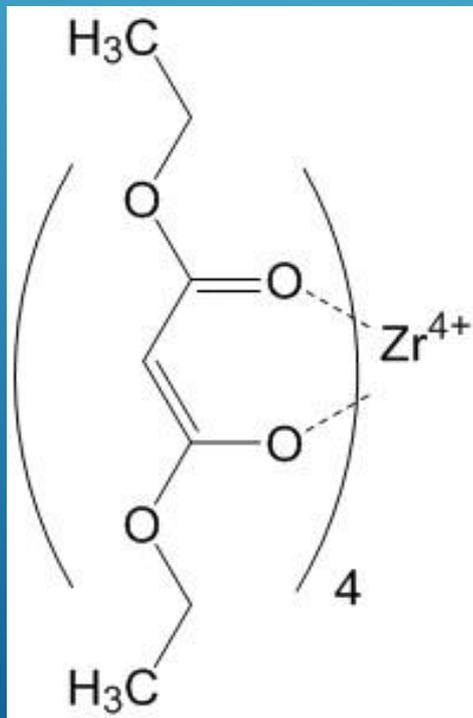
Some impurities containing in regular anisole (same as acetonitrile) dissolved β-keto ester complex.

FID結果 Pk #	名前	保持時間	面積	面積%	ヘーラインコード
1		1.63	406	0.013	BV
2		1.72	38	0.001	VV
3		1.77	830	0.027	VV
4		1.89	22	0.001	VV
5		2.03	34	0.001	VB
6		2.27	23	0.001	BV
7		2.37	128	0.004	VB
8	anisole	3.01	38	0.001	BB
9		3.15	46	0.001	BB
10		4.11	3105380	99.725	BB
11		5.11	2066	0.066	BB
12		5.58	35	0.001	BB
13		5.69	25	0.001	BB
14		5.93	74	0.002	BB
15		6.17	2671	0.086	BB
16		6.44	193	0.006	BB
17		6.73	1560	0.050	BB
18		8.87	360	0.012	BB

# TETRAKIS (DIETHYL MALONATO) ZIRCONIUM AND ABSORBANCE SPECTRUM OF LIGAND



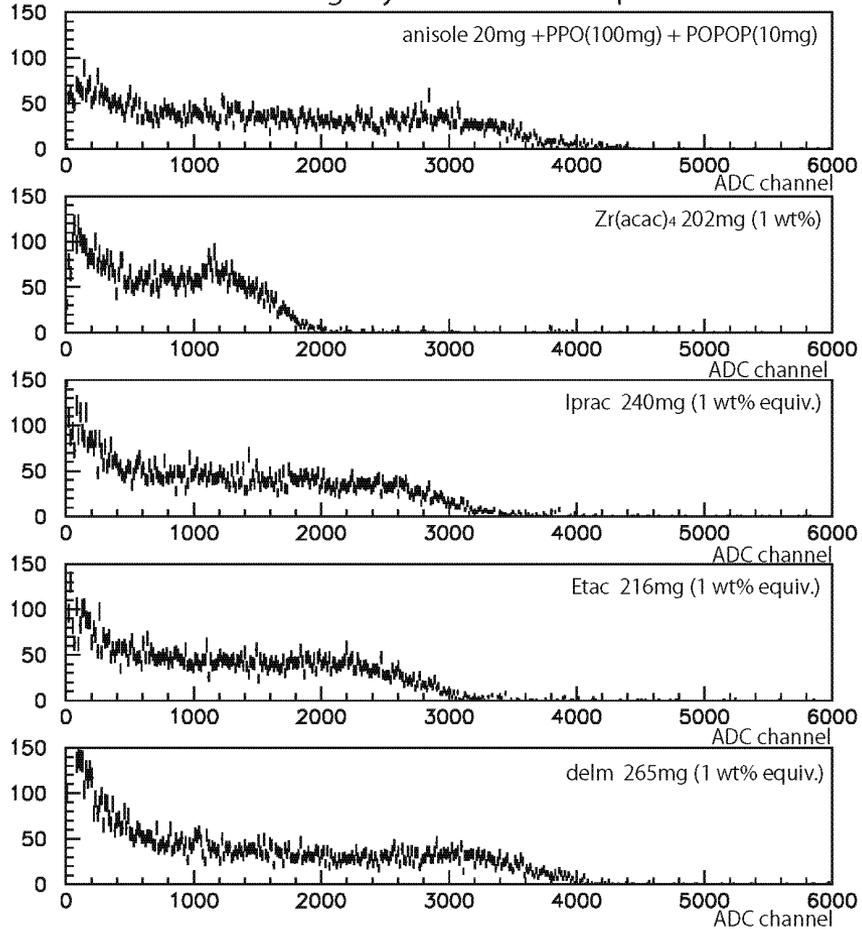
mw : 727.84



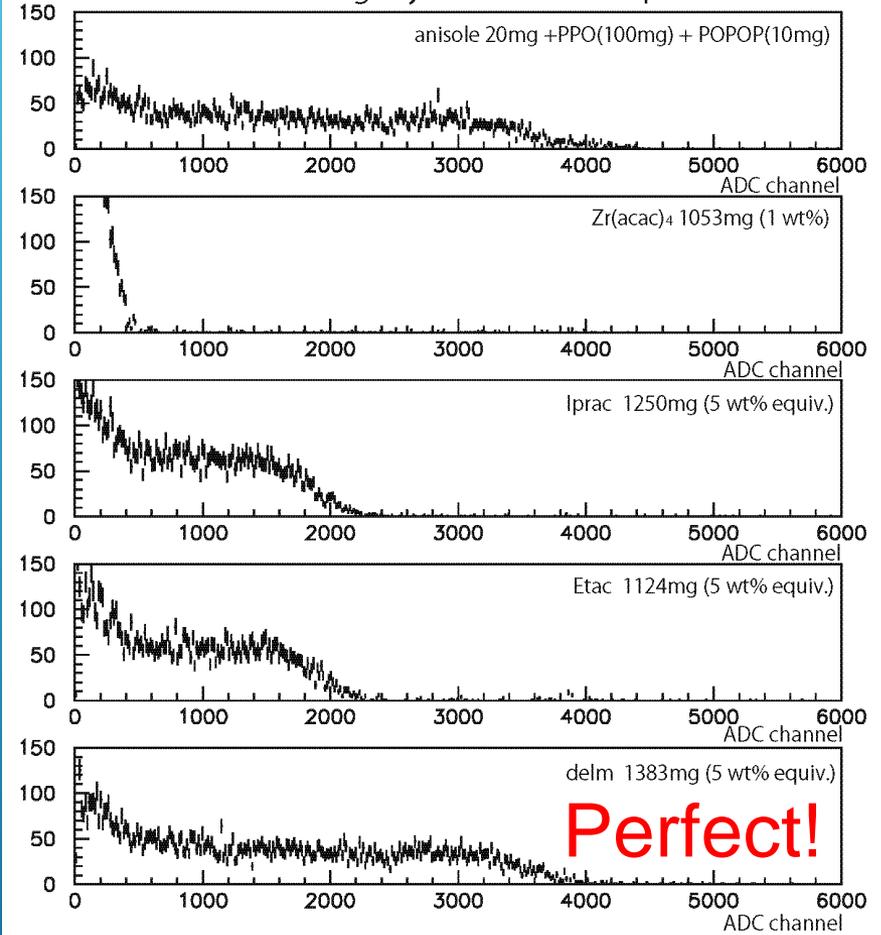
**shorter wavelength (~210nm)**

# LIGHT YIELD OF LS CONTAINING DIEHYL MALONATE LIGAND (WITH PURE ANISOLE)

Scintillation light yield for 1wt% equivalent



Scintillation light yield for 5wt% equivalent

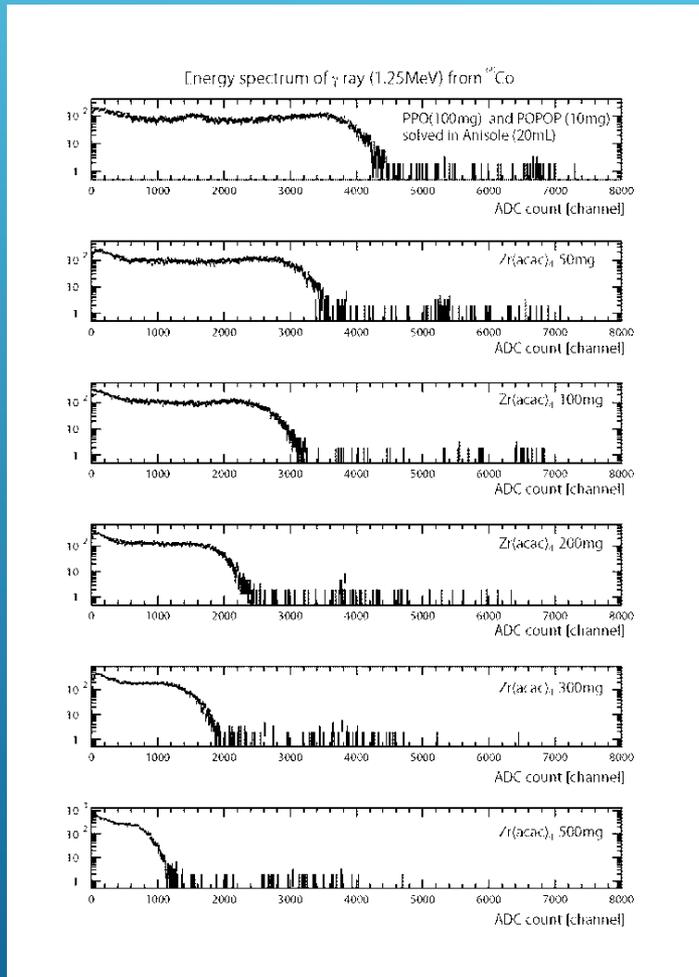


# SUMMARY

- ▶ Confirmed absorption peak moved to shorter wavelength (275nm → 245nm) by introducing  $\beta$ -keto ester substituent groups.
- ▶ Polar solvent and impurities could dissolve  $\beta$ -keto ester complex and no effect to shorten wavelength.
- ▶ Pure anisole does not dissolve  $\beta$ -keto complex.
- ▶ tetrakis (diethyl malonato) zirconium should be an ultimate complex for resolving zirconium in liquid scintillator.

# BACKUP

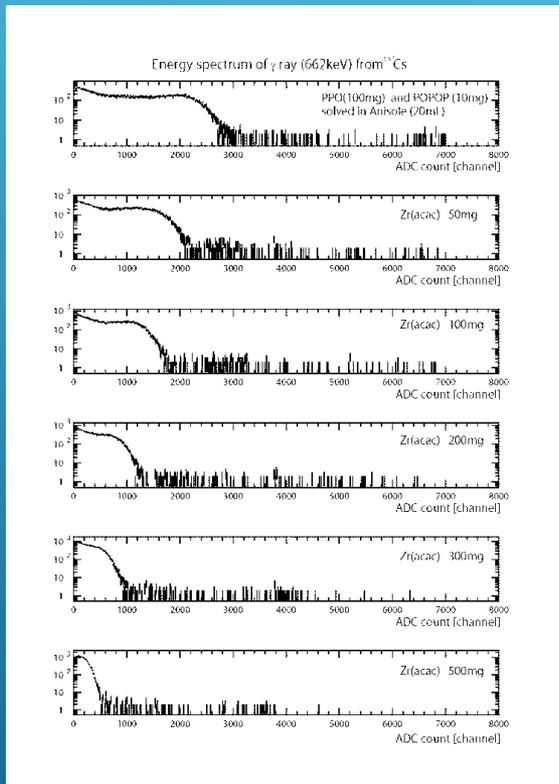
# SCINTILLATION LIGHT YIELD WITH RESPECT TO CONCENTRATION OF ZIRCONIUM COMPLEX



concentration of Zr(acac) <sub>4</sub>	Observed channel	Expected channel
0 mg	3850	3850
50mg (1.03X10 <sup>-4</sup> )	3175	3138
100mg (2.05X10 <sup>-4</sup> )	2800	2651
200mg (4.10X10 <sup>-4</sup> )	2000	2018
300mg (6.15X10 <sup>-4</sup> )	1600	1613
500mg (1.03X10 <sup>-3</sup> )	900	1178

**PPO 100mg : 4.52X10<sup>-4</sup> mol**

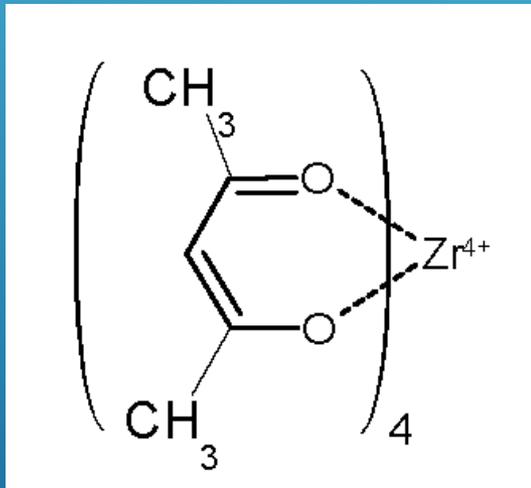
# SCINTILLATION LIGHT YIELD ( $^{137}\text{Cs}$ ) WITH RESPECT TO CONCENTRATION OF $\text{Zr}(\text{ACAC})_4$



concentration of $\text{Zr}(\text{acac})_4$	Observed channel	Expected channel
0 mg	2450	2450
50mg	1800	1997
100mg	1400	1687
200mg	950	1284
300mg	650	1038
500mg	300	750

# ZIRCONIUM B-DIKETON COMPLEX

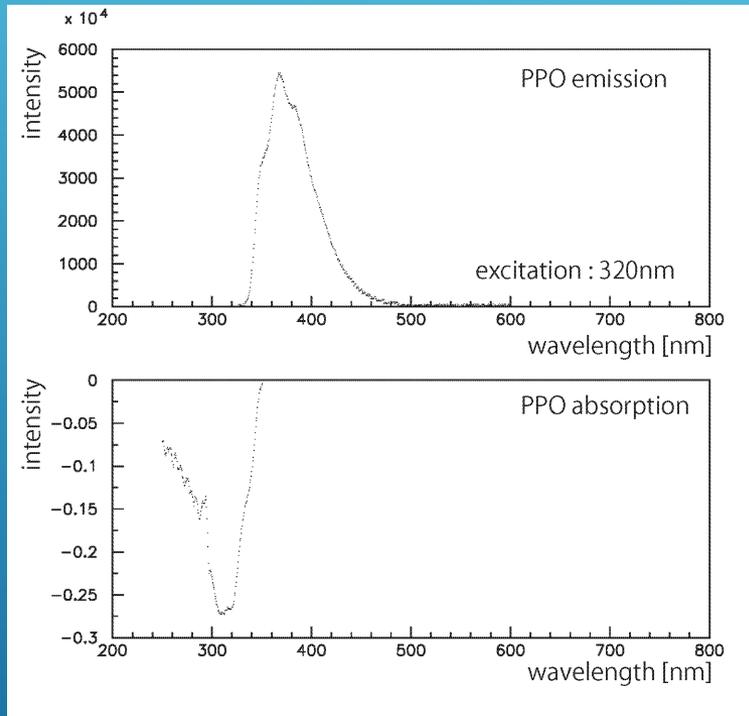
- ▶ Zirconium(IV) acetylacetonate ( $\text{Zr}(\text{acac})_4$ )



- ▶ Advantage
  - ▶ good solubility (over 10w.t.%) in Anisole (PhOMe)
  - ▶ Stable and cheap
  - ▶ Commercial product
- ▶ Disadvantage
  - ▶ **Low scintillation light yield**

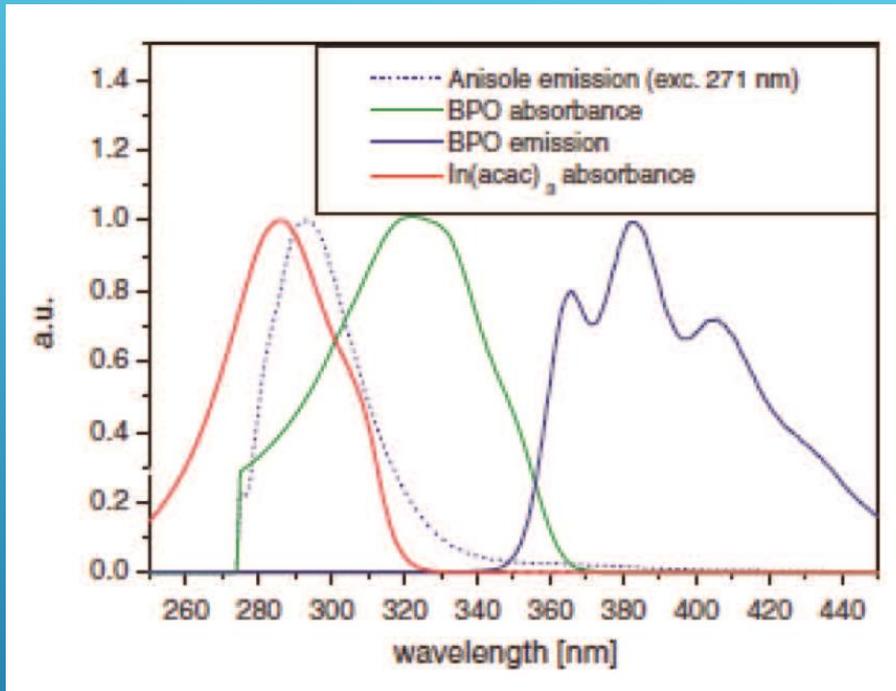
Molecular weight : 487.66

# 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

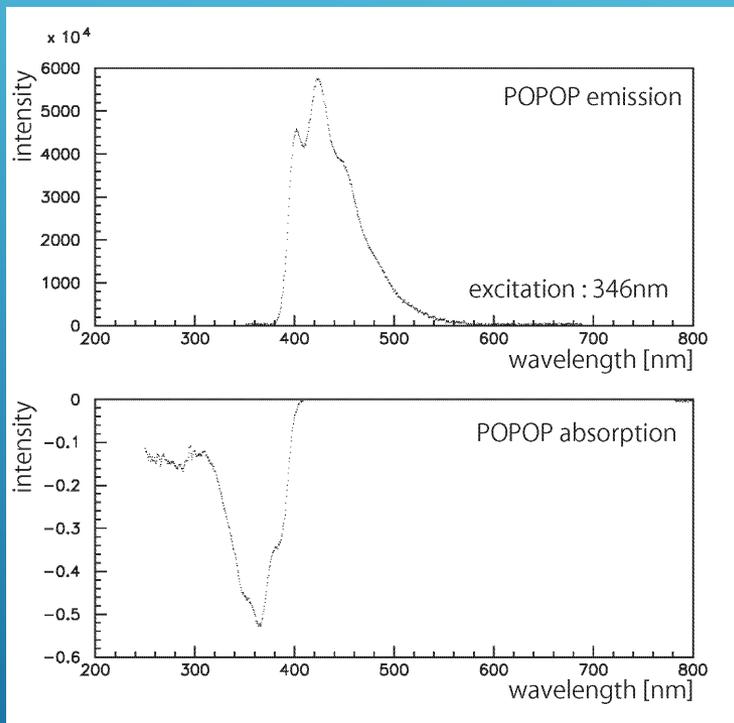
# WHAT'S PROBLEM



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

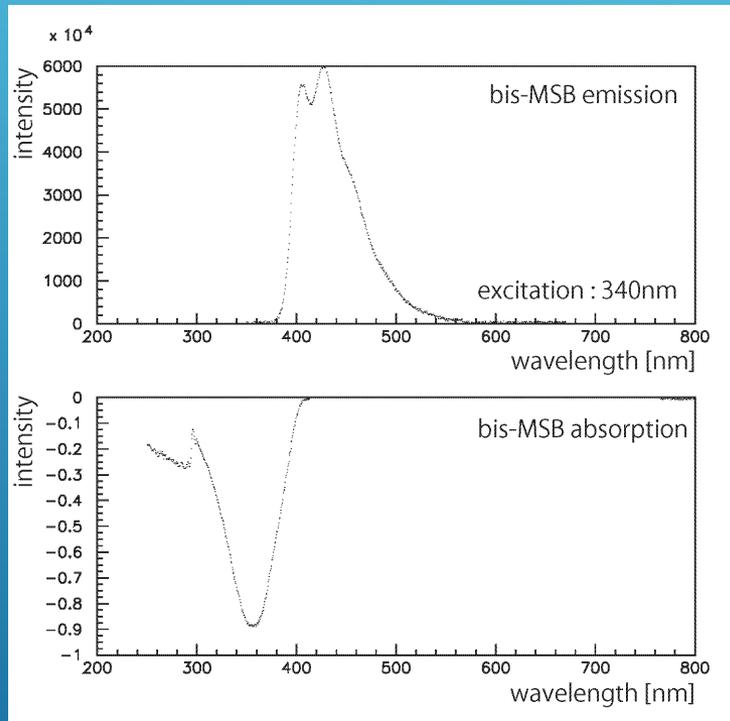
Same overlap between the emission and the absorption could be occurred even if different metal (Zr) was used.

# 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

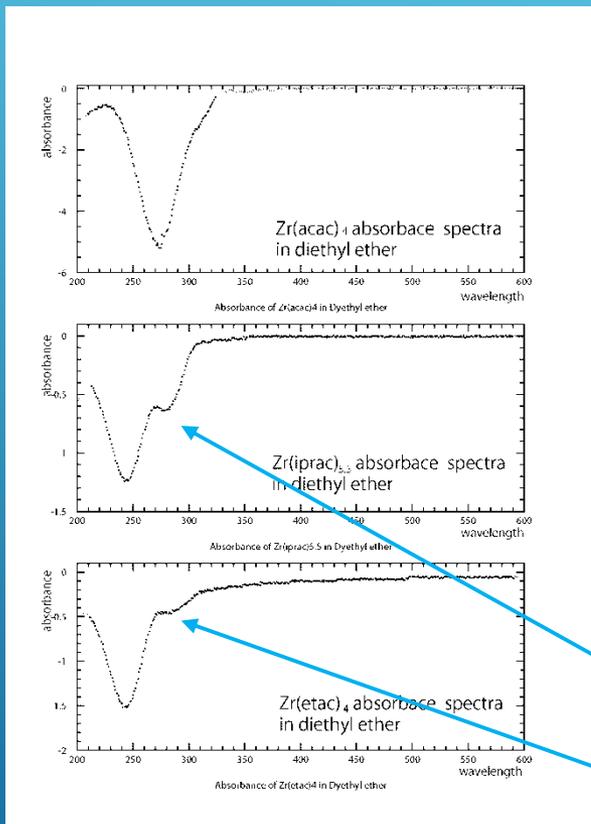


## ▶ Photo luminescence

- 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

# ABSORBANCE IN LIQUID SCINTILLATOR

## SOLUTION : DIETHYL ETHER

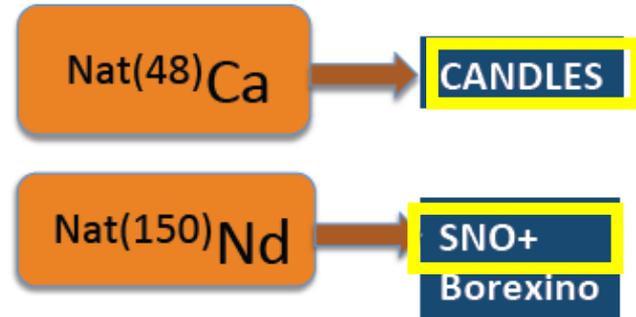
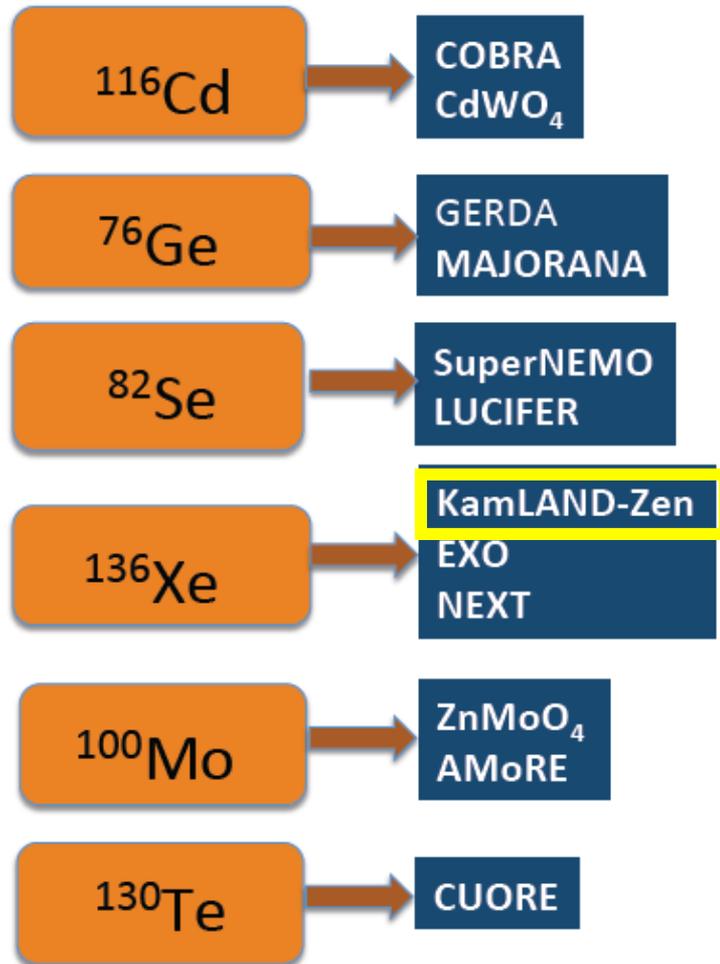


- ▶ Two absorption peaks were found in diethyl ether.
- ▶ It could be explained by part of dissolving  $\beta$ -keto ester complex.
- ▶ Two components could coexist of speed of dissolving could be slow.

**Additional peak was found around 270nm**

# Studied isotopes

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## A dream ?

