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Purification of lanthanides for double beta decay experiments

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1. Motivation

There are many potentially double beta active isotopes among the lanthanide elements:

- ^{136}Ce, ^{138}Ce, ^{142}Ce;
- ^{146}Nd, ^{148}Nd, ^{150}Nd;
- ^{144}Sm, ^{154}Sm;
- ^{152}Gd, ^{160}Gd,
- ^{156}Dy, ^{158}Dy;
- ^{162}Er, ^{164}Er, ^{170}Er,
- ^{168}Yb, ^{176}Yb.

Transition	Energy release, $Q_{2\beta}$, keV [1]	Isotopic abundance, % [2]	Decay channel [3]
^{136}Ce → ^{136}Ba	2378.55(27) [4]	0.185(2)	2ε, εβ$^+$, 2β$^+$
^{138}Ce → ^{138}Ba	693(10)	0.251(2)	2ε
^{142}Ce → ^{142}Nd	1417.2(21)	11.114(51)	2β$^-$
^{144}Sm → ^{144}Nd	1782.4(8)	3.07(7)	2ε, εβ$^+$
^{154}Sm → ^{154}Gd	1250.8(9)	22.75(29)	2β$^-$
^{146}Nd → ^{146}Sm	70.5(28)	17.189(32)	2β$^-$
^{148}Nd → ^{148}Sm	1928.3(19)	5.756(21)	2β$^-$
^{150}Nd → ^{150}Sm	3371.38(20)	5.638(28)	2β$^-$
^{152}Gd → ^{152}Sm	55.68(18)	0.20(1)	2ε
^{160}Gd → ^{160}Dy	1730.5(13)	21.86(19)	2β$^-$
^{156}Dy → ^{156}Gd	2005.95(10)	0.056(3)	2ε, εβ$^+$
^{158}Dy → ^{158}Gd	282.7(25)	0.095(3)	2ε
^{162}Er → ^{162}Dy	1846.96(30)	0.139(5)	2ε, εβ$^+$
^{164}Er → ^{164}Dy	25.07(11)	1.601(3)	2ε
^{170}Er → ^{170}Yb	655.6(17)	14.910(36)	2β$^-$
^{168}Yb → ^{168}Er	1409.27(25)	0.123(3)	2ε, εβ$^+$
^{176}Yb → ^{176}Hf	1088.7(18)	12.996(83)	2β$^-$

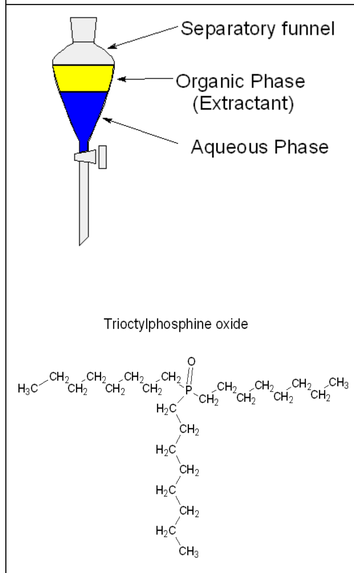
^{136}Ce is one of only six potentially 2β$^+$ active nuclei with promising theoretical predictions for double beta decay half-lives on the level of 10^{18} - 10^{22} yr.
Gadolinium has two promising nuclei: 1) **^{152}Gd** where resonant neutrinoless double electron capture is possible with the half-life on the level of 8×10^{23} – 8×10^{26} yr for the effective neutrino mass 1 eV; and 2) **^{160}Gd** with high isotopic abundance (21.9%) and promising theoretical predictions for 0ν2β$^-$ channel.
^{150}Nd is interesting nuclei to search for 0ν2β decay thanks to high 2β energy of decay (3368 keV) and isotopic abundance (5.6%), promising theoretical estimations.

2. Purification of cerium, neodymium, and gadolinium oxides

Even high purity grade (99.99% - 99.995%) lanthanide compounds contain uranium and thorium typically on the level of ~ (0.1 – 1) Bq/kg.

The samples of CeO_2, Nd_2O_3, Gd_2O_3 were purified by physical and chemical methods. The same procedures were applied for gadolinium and neodymium purification because of very similar chemical properties. A slightly different approach was utilized to purify cerium since this element has chemical properties very close to thorium and rather different to other lanthanides.

Purification procedure	
Neodymium and Gadolinium	**Cerium**
Dissolving of oxides	
Nd_2O_3 and Gd_2O_3 were dissolved in acid solution (HCl of super pure quality grade): $Nd_2O_3(Gd_2O_3) + 6HCl \rightarrow 2NdCl_3(GdCl_3) + 3H_2O$ Initial amounts of lanthanide oxides and hydrochloric acid were calculated so that to obtain final solution with concentration of $NdCl_3(GdCl_3)$ 20% and pH ≤ 0.1	A mixture of concentrated nitric and hydrofluoric acids was used to dissolve CeO_2 : $2CeO_2 + 4HNO_3 + 4HF \rightarrow Ce(NO_3)_4 + CeF_4\downarrow + 4H_2O$ Some part of cerium was lost due to formation of insoluble cerium fluoride. Initial amounts of CeO_2 and HNO_3 were calculated so that to obtain solution with concentration of $Ce(NO_3)_4$ 10% and 5 mol/L of nitric acid



Liquid-liquid extraction

Liquid-liquid extraction technique was used to purify the obtained aqueous solutions from thorium and uranium. Liquid-liquid extraction is a method by which a compound is pulled from solvent A to solvent B while solvents A and B are not miscible.

Aqueous solution of lanthanides were taken as solvents A, while phosphor-organic complexing compound trioctylphosphine oxide (TOPO) in toluene was used as solvent B.

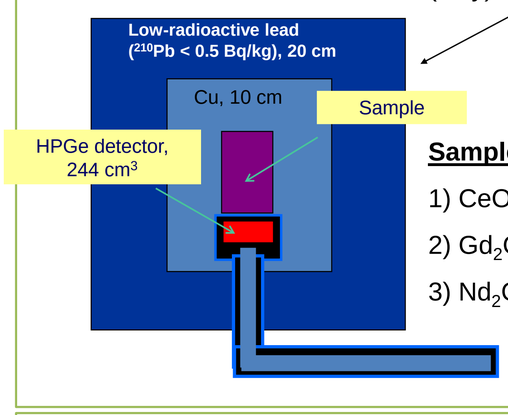
At these conditions elements with a higher oxidation move to organic phase with a higher distribution level than elements with lower oxidation. It allows to reach some positive effect to separate the elements with different oxidation states [6].

The liquid-liquid extraction was realized using a separatory funnel.

Extraction of Th and U from Nd and Gd	**Extraction of Ce**
Solvent A: 20% acidic solution of gadolinium or neodymium chloride. We have used TOPO with concentration 0,1 mol/L as solvent B. $LnCl_3(Th, U)_{(aq)} + nTOPO_{(org)} \rightarrow \rightarrow LnCl_{3(aq)} + [(Th, U)\bullet nTOPO](Cl)_{x(org)}$ Ln – Nd, Gd	Solvent A: solution of $Ce(NO_3)_4$ with high content of nitric acid. Solvent B: 33% solution of TOPO in toluene. $Ce(NO_3)_{4(aq)} + nTOPO_{(org)} \rightarrow [Ce\bullet nTOPO](NO_3)_{4(org)}$ *Efficiency of cerium extraction was very low due to the lack of TOPO content in solvent B*

3. Radioactive contamination of samples measured with the HP Ge γ spectrometry

The radioactive contamination of the samples **before** and **after** the purification was tested by using ultra-low-background HPGe gamma spectrometry at the underground Gran Sasso National Laboratories of the INFN (Italy).

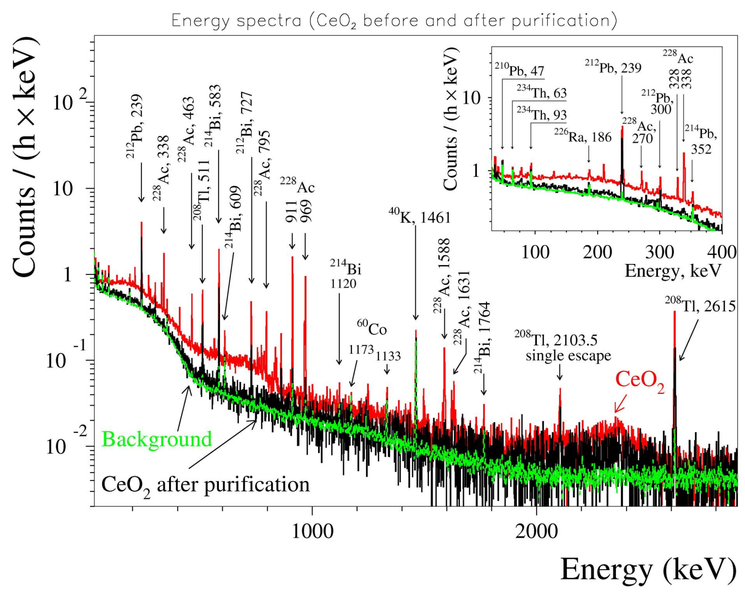


Scheme of the measurements with the GeBer HPGe detector (244 cm^3). Passive shield: Cu, Pb and polyethylene
Energy resolution ~ 2 keV @1333 keV (^{60}Co)

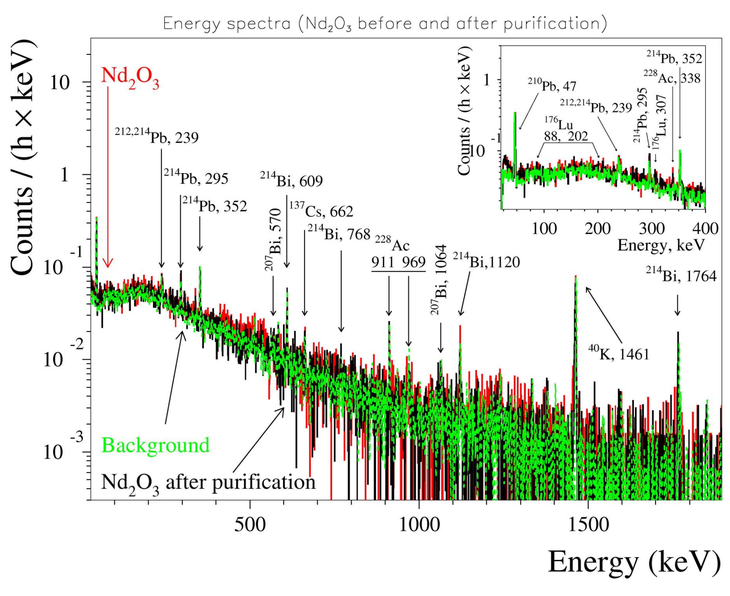
Samples:

1) CeO_2 (501 g, 893 h → 98 g, 397 h), GeBer (244 cm^3)
2) Gd_2O_3 (491 g, 942 h → 495 g, 995 h), GeBer (244 cm^3)
3) Nd_2O_3 (377 g, 631 h → 374 g, 665 h), GePaolo (518 cm^3)

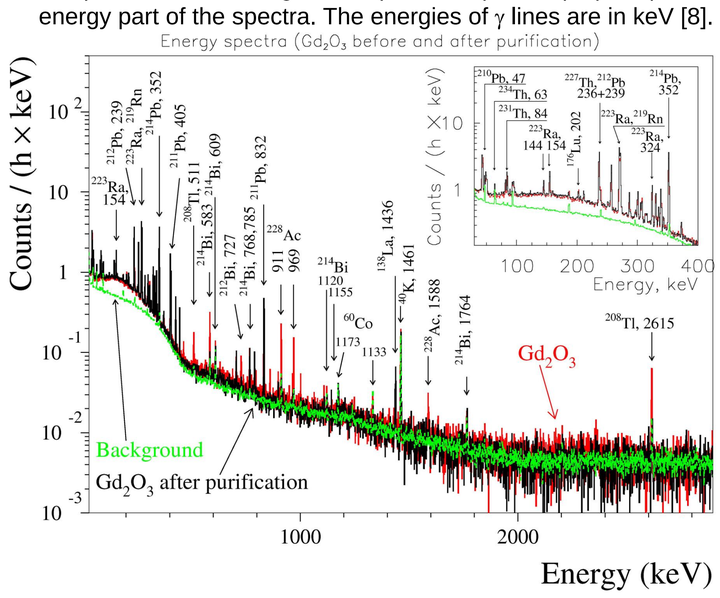
Detection efficiency has been simulated with the help of the GEANT4 code [5]



Energy spectra of the CeO_2 samples measured by HPGe detector (GeBer) before (893 h) and after (397 h) purification in comparison with background spectrum (6110 h). (Inset) Low energy part of the spectra. The energies of γ lines are in keV [8].



Energy spectra of the Nd_2O_3 samples measured by HPGe detector (GePaolo) before (631 h) and after (665 h) purification in comparison with background spectrum (1528 h). (Inset) Low energy part of the spectra. The energies of γ lines are in keV [8].



Energy spectra of the Gd_2O_3 samples measured by HPGe detector (GeBer) before (942 h) and after (995 h) purification in comparison with background spectrum (6110 h). (Inset) Low energy part of the spectra. The energies of γ lines are in keV [8].

Chain		Activity, mBq/kg					
		CeO_2		Gd_2O_3		Nd_2O_3	
		before	after	before	after	before	after
^{232}Th	**^{228}Ra**	**850(50)**	**72(18)**	**106(10)**	**<12**	<2.1	<2.6
	^{228}Th	620(30)	620(40)	**79(6)**	**<4**	<1.3	<1.0
^{238}U	**^{234}Th**	<590	<790	<1100	<670	<28	<46
	^{234m}Pa	<870	<4600	<1000	<590	<46	<27
	^{226}Ra	**11(3)**	**<9.3**	<7.4	<8.3	<2.8	<1.8
^{235}U	**^{235}U**	38(10)	<24	**96(12)**	**<8.3**	<1.7	<1.3
	^{231}Pa	---	---	**1390(60)**	**1920 (80)**	---	---
	^{40}K	**77(28)**	**<240**	**<80**	**<35**	<29	<15
	^{137}Cs	<3.0	<8.5	<6	<3.8	<0.80	<0.53
	^{60}Co	<1.2	<4.4	<1.1	<1	<0.21	<0.40
	^{176}Lu	---	---	32(3)	30(3)	1.1(4)	<1.3
	^{138}La	---	---	12(2)	26(3)	---	---

Re-extraction (for Cerium only)

Re-extraction of cerium from organic phase was performed into low acidic water solution with a simultaneous decreasing of the Ce oxidation level. Hydrogen peroxide was utilized as reducing agent.

$2[Ce\bullet nTOPO](NO_3)_{4(org)} + H_2O_2 \rightarrow 2Ce(NO_3)_{3(aq)} + 2HNO_3 + O_2 + 2nTOPO_{(org)}$

Some part of cerium left in organic phase

Precipitation of Ce, Nd and Gd hydroxides

Further purification and separation of lanthanides was carried out with the precipitation of the hydroxides at increasing pH level up to 7 [7]:

$Nd(Gd)Cl_3 + 3NH_3 + 3H_2O \rightarrow Nd(Gd)(OH)_3\downarrow + 3NH_4Cl$

At the same time the oxidation level of cerium has been increased due to the excess of hydrogen peroxide:

$2Ce(NO_3)_3 + 6NH_3 + H_2O_2 + 6H_2O \rightarrow 2Ce(OH)_4\downarrow + 6NH_4NO_3$

The obtained amorphous sediments were rinsed several times by ultrapure water and placed into quartz backers for drying and annealing.

Recovering of CeO_2, Nd_2O_3 and Gd_2O_3 samples

High temperature decomposition of hydroxides $Nd(Gd)(OH)_3$ and $Ce(OH)_4$ was used for stoichiometric oxides CeO_2, Nd_2O_3 and Gd_2O_3 formation.

The output of the purified oxides were: ~ 90% for Nd_2O_3 and Gd_2O_3
~ 20% for CeO_2

4. Conclusions

- Liquid-liquid extraction technique was used to purify CeO_2, Nd_2O_3 and Gd_2O_3
- Gd_2O_3 has been purified most effectively: radioactive contamination was decreased to 0.004 Bq/kg in ^{228}Th, to <0.008 Bq/kg in ^{226}Ra, and to 0.04 Bq/kg in ^{40}K.
- The purification methods are much less efficient for chemically very similar radioactive elements like lanthanum and lutetium.
- Further R&D of purification methods and preparation of experiments to search for 2β decay of several lanthanide isotopes are in progress.

References

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