

The 3rd INFN School on Underground Physics







MATERIAL SCREENING

Monica Sisti **INFN Milano-Bicocca**



18 October 2024

OUTLINE

- Sources of radioactive background
- The strategies for background reduction
- The main techniques for material screening:
 - Gamma spectroscopy with HPGe detectors
 - Neutron activation analysis
 - Inorganic mass spectrometry
 - Alpha spectroscopy
 - "Custom" techniques



RADIOACTIVITY IS ALL AROUND US

SOURCES OF HUMAN RADIATION EXPOSURE AVERAGE CONTRIBUTIONS IN ITALY:

- Natural radiation (~80%)
 - Radon gas: 1.5 2.5 mSv/y
 - Cosmic radiation: 0.3 0.5 mSv/y
 - Terrestrial radiation: 0.3 0.4 mSv/y
 - Internal radiation: 0.2 mSv/y
- Artificial radiation (~20%)
 - Medical procedures: 0.5 1.2 mSv/y
 - Other sources: negligible
- Total Average Annual Radiation Exposure in Italy: ~ 3 4 mSv/y





THE CUORE EXPERIMENT WITH CRYOGENIC DETECTORS



A CASE STUDY - $0\nu\beta\beta$ decay search

A CASE STUDY - $0\nu\beta\beta$ decay search

PLANNED AND FUTURE EXPERIMENTS







A CASE STUDY - MEASUREMENT OF γ oscillations

THE JUNO EXPERIMENT TO DETERMINE THE NEUTRINO MASS ORDERING



iment	Daya Bay	BOREXINO	KamLAND	JUNO
nass	20 ton	~ 300 ton	~ 1 kton	20 kto
erage	~ 12%	~ 34%	~ 34%	~ 78%
esolution	~ 8% /√E	~ 5% /√E	~ 6% /√E	~ 3% /v
yield	~ 160 p.e. /MeV	~ 500 p.e. /MeV	~ 250 p.e. /MeV	> 1345 p.e.



A CASE STUDY - JUNO RADIOPURITY REQUIREMENTS

FOR THE LIQUID SCINTILLATOR (20 KTON OF MASS)

Minimum requirements for LS:

- $238U/232Th < 10^{-15} g/g$
- $40 \text{K} < 10^{-16} \text{ g/g}$



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⁴⁰K content ~3.6×10⁻⁷ g/g

JUNO LS ⁴⁰K content < 10⁻¹⁶ g/g

illustrative only! not to scale!







SOURCES OF RADIOACTIVITY

OF PARTICULAR CONCERN FOR NEUTRINO AND DARK MATTER EXPERIMENTS

- secular equilibrium and ⁴⁰K
- Natural medium lived radionuclides ²²⁶Ra, ²¹⁰Pb/²¹⁰Bi, ²¹⁰Po when secular equilibrium is broken in ²³⁸U chain
- Gaseous nuclides ²²²Rn, ⁸⁵Kr, ...
- Cosmic rays
- Cosmogenic activated nuclides

• Natural long lived radionuclides ²³⁸U and ²³²Th - with their decay chains at

Artificial (anthropogenic, man-made) radionuclides ⁶⁰Co, ¹³⁷Cs, ³H, ¹⁴C, ⁹⁰Sr, ...



COSMIC RAYS

PRIMARY AND SECONDARY COMPONENTS

- Primary cosmic rays: protons (90%), alphas (9%), heavier nuclei (1%)
- Secondary particles produced by interaction with atmosphere: neutrons, electrons, neutrinos, protons, muons, pions
- Muons and neutrons are of great concern in low background experiments

Meter of water equivalent (m.w.e.) represents the thickness of water that would provide the same level of shielding as the given material





COSMIC RAYS

MUON ATTENUATION IN UNDERGROUND LABORATORIES

- Muon flux at sea level: ~ 10⁻² cm⁻² s⁻¹
- The energy spectrum of muons is shifted towards higher energies with increasing depth: ~ 4 GeV at sea level
 - ~ 270 GeV at LNGS
- Muon spallation products could be difficult to tag: neutrons are of most concern

 10^{-10} European facilities LSC Yemilab Mountain overburden 10^{-7} Kamioka Boulby **SUPL** LNGS CallioLab 10^{-8} LSM ▲ Baksan **SURF** 10^{-9} 10^{-10} 3 5 4 6 Depth [km w.e.]





COSMIC RAYS

MUON ATTENUATION IN UNDERGROUND LABORATORIES

•	Muon flux at sea level:		
	~ 10 ⁻² cm ⁻² s ⁻¹		0
•	The energy spectrum of muons is shifted towards higher energies with	(m.w.e.) ר	-2000
	increasing depth: ~ 4 GeV at sea level ~ 270 GeV at LNGS	oratory Depth	-4000
•	Muon spallation products could be difficult to tag:	Lab	-6000
	neutrons are of most concern		-8000





NEUTRON PRODUCTION UNDERGROUND

FROM NATURAL RADIOACTIVITY: (α , n) REACTIONS AND SPONTANEOUS FISSION

					IReprodu	iced from 2.]
	U (ppm)	Th (ppm)	$\mathbf{U}(\boldsymbol{\alpha}, \boldsymbol{n})$	$Th(\alpha, n)$	Fission	
Type of rock Concentration (ppm)		(neutrons/g/y)			Total yield	
Granite	5	11	7.85	7.755	2.33	17.9
Limestone	1	1	0.64	0.285	0.467	1.4
Sandstone	1	1	0.837	0.38	0.467	1.7
Granite A	1.32	7.79	2.24	5.92	0.62	8.8
Granite B	6.25	4.59	10.62	3.49	2.92	17.0
Granite C	1.83	4.38	3.11	3.33	0.85	7.3
Salt I	0.30	2.06	1.60	4.77	0.14	6.5
Salt II	0.13	1.80	4.17	0.69	0.06	4.9

Estimated neutron production from different types of rocks

control is crucial.

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• U/Th contaminations in the detector materials could also be a source of (α, n) reactions, e.g. natural contaminants in the liquid scintillator of JUNO: material



COSMOGENIC ACTIVATED NUCLIDES

RADIOISOTOPE PRODUCTION

- Production of different radionuclides depending on the materials under
- e.g., Measured activated nuclides in copper:



consideration. This is of concern for all components of the experimental setup.

[Applied Radiation and Isotopes 67 (2009) 750-754]

ıclide	Half-life ^a	(Saturation) a	Saturation) activity (μ Bq kg ⁻¹)		
		Exposed	Unexposed	Estimated ^b	
enic					
	77.236 d	230 ± 30		557	
	271.80 d	$1800\!\pm\!400$		2147	
	70.83 d	1650 ± 90		3878	
	5.271 a	2100 ± 190	<10	2367	
	312.13 d	$215\!\pm\!21$		791	
	44.495 d	455 ± 120		157	
	83.788 d	$53\!\pm\!18$		93	
	15.9735 d	110 ± 40			
ial					
J)	1600 a	<35	<16		
`h)	698.60 d	<20	<19		
	$1.265 \times 10^9 \mathrm{a}$	<110	<88		



ANTHROPOGENIC RADIONUCLIDES

- Radioactive isotopes occurring in the environment due to human activities
- They are mostly the results of nuclear weapons testing, nuclear accidents, and operation of nuclear power plants.
- The most dangerous nuclides depend on the particular experiment and on the environment, e.g. ^{108m}Ag for KamLAND-ZEN after the Fukushima accident.

Very dangerous are the pure beta emitters like 90 Sr (T_{1/2} = 28.9 y, Q=546 keV), e.g. for $2\nu\beta\beta$ studies.

MAN-MADE RADIOACTIVITY



NATURAL RADIOACTIVITY

²³⁸U AND ²³²TH SERIES:



Average concentrations in the Earth's crust:

- ²³⁸U ~ 36 Bq/kg
- ²³²Th ~ 44 Bq/kg
- ⁴⁰K ~ 850 Bq/kg





NATURAL RADIOACTIVITY

²³⁸U SERIES

equilibrium breaking points

- ²³⁸U: i.a. 99.3% half-life 4.5×10⁹ y
- Decay chain is rarely in secular equilibrium
- One of its daughters, ²²²Rn, is responsible for most of the human radiation exposure. It is also one of the most insidious background sources.
- Radon decay is the origin of ²¹⁰Pb (²¹⁰Po) implantation on material surfaces.









NATURAL RADIOACTIVITY

²³²TH SERIES

equilibrium breaking points

- ²³²Th: i.a. 100% half-life 14×10⁹ y
- The decay chain quickly reaches secular equilibrium, typically within approximately 30 years.
- The radon isotope in the thorium decay chain has a significantly shorter half-life compared to ²²²Rn.





BACKGROUND REDUCTION

THE EVERYDAY STRUGGLE OF A LOW-BACKGROUND EXPERIMENTALIST

- Environmental radioactivity
- Contaminations in the shielding material
- Contaminations in the detector material
- Radon and its progenies
- Cosmic and cosmogenic background











Low background γ -ray spectroscopy

USING HIGH PURITY GERMANIUM DETECTORS (HPGE)

- Semiconductor p-i-n diodes: under reverse bias an electric field extends across the intrinsic (depleted) region
- When photons interact within the depleted region, charge carriers are produced and swept by the electric field to the electrodes. The charge is proportional to the deposited energy
- Since germanium has a small band gap (—> superior energy resolution), the detector must be operated at 77°K to reduce leakage current



19

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[credits: P. Loaiza]





REDUCING ENVIRONMENTAL, COSMIC AND COSMOGENIC BACKGROUND



- Passive background reduction:
- Pb (high Z) is usually a good choice



21

SHIELDING MATERIAL RADIOPURITY

COMPOSITE SHIELDING IS USUALLY USED

material	activity [µBq/kg]				
	²²⁶ Ra (U)	²²⁸ Th (Th)	⁴⁰ K	various	
lead	≤ 29 °)	≤ 22 ^{α)}	270 ^{a)}	< 4x10 ³ ²¹⁰ Pb ^{b)}	28.5
copper	≤ 16 °)	9 ^{c)} ≤ 19 ^{a)}	≤ 88 °)	≤ 10 ⁶⁰ Co ^{α)}	40.9
steel	130 ^{a)}	≤ 40 °)	50 ^{a)}	140 ⁶⁰ Co ^{a)}	46.2
water	≤ 1 *	0.04 ^{d)} 0.008 ^{e)}	≤ 2 ^{d)}		324
liq. sc. (PC)	10 ^{-6 f)}	\leq 10 ^{-6 f)}	≤ 0.001 ²	F)	373
liq. nitrogen	≤ 0.3*			10 ^{-3 39} Ar ^{g)} 0 04 ⁸⁵ Kr ^{g)}	443
liq. argon	≤ 7*			39 Ar: 10 ^{6 h)} 6500 ⁱ⁾	276
liq. xenon	<< 60 ^{k)} *			0.2 ⁸⁵ Kr ^{k)+}	120

^{a)} GeMPI; ^{b)} bolometric Milano; ^{c)} Ge PNNL; ^{d) 232}Th by ICP-MS Ispra; ^{e) 232}Th by NAA TU München; ^{f) 226}Ra + ²²⁸Th by Bi-Po Borexino; ^{g)} Rare Gas MS MPI-K; ^{h)} atmospheric Ar, PC Bern, WARP; ⁱ⁾ underground Ar, I. Xu et al. (DarkSide), ^{j)} Gerda; ^{k)} XENON100/1T ,⁺ Rare Gas MS MPI-K; * via ²²²Rn MPI-K

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5 cm

9 cm

2 cm

cm

cm

cm

cm

cm



BEGe @ Milano-Bicocca



Roman lead





ENVIRONMENTAL BACKGROUND REDUCTION BY SHIELDING



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[credits: G. Heusser]









REDUCING ENVIRONMENTAL, COSMIC AND COSMOGENIC BACKGROUND

Geγ-spectra of Rn progenies on a plastic foil at different time intervals after plate-out (after evacuating the sample chamber): the first 130 min (top); 200-1500 min (middle); 2-22 days (bottom)



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To reduce Rn:

- Enclose the shielding and flush with nitrogen gas
- Pump the sample chamber



GIOVE (GERMANIUM INNER OUTER VETO) AT 15 M.W.E.



Fig. 1 Cut-away view of the GIOVE detector and shield. Different layers for radiation absorption (Pb, Cu), neutron moderation (PE) and active vetoing (*red colored areas*) form a shell structure to efficiently lower the background count rate in the central Ge crystal. More details provided in the text

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Table 5 Integral count rates of low-background Ge spectrometers located in different underground sites. The values are normalized by the active mass (m_{act}) of the detectors. Among them, only GIOVE

and Corrado are equipped with active muon veto systems. The sample chambers (SC) were empty during the measurement

m _{act} (kg)	SC _{vol} (liter)	Location, depth (m w.e.)	μ flux reduction (comp. sea level)	Co (40 (d ⁻
1.81	12.4	MPIK, 15	2-3	348
0.94	11	MPIK, 15	2-3	366
1.24	0.4	HADES, 500	5×10^{3}	394
2.06	15	LNGS, 3800	10^{6}	66
$\begin{bmatrix} 10^{8} \\ 10^{7} \\ 10^{6} \\ 10^{5} \\ 10^{6} \\ 10^{3} \\ 10^{4} \\ 10^{2} \\ 10^{-1} \\ 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \\ 0 \end{bmatrix}$	<pre></pre>		2000 2500 Energy [keV]	





REDUCING BACKGROUND FROM DETECTOR MATERIAL COMPONENTS

- Optimize design
- Select materials



GeMPI detector at LNGS [Heusser, Laubenstein]



BACKGROUND CONTROL IN \nu/DM EXPERIMENTS

EXAMPLE: THE JUNO DETECTOR

• Optimize design • Select materials







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Detailed Monte Carlo simulations of the experimental apparatus — with all materials included — are needed to build the expected Background Budget of the experiment







BACKGROUND CONTROL IN \nu/DM EXPERIMENTS

EXAMPLE: THE JUNO DETECTOR



Optimize design Select materials







BACKGROUND CONTROL IN \nu/DM EXPERIMENTS

EXAMPLE: THE JUNO DETECTOR



Optimize design Select materials







HOW TO ASSESS THE CONCENTRATION OF A CONTAMINANT IN A MATERIAL

N = number of atoms of the radioactive species R with life-time $\tau = 1/\lambda$

Concentration measurement

$$N_{mis} = N(t) \simeq N(t + \Delta t)$$

$$N(t) \neq N(t + \Delta t)$$

$$N_{mis}$$

MEASURING RADIOACTIVITY





N = number of atoms of the radioactive species R with life-time $\tau = 1/\lambda$

Concentration measurement

The decision between a concentration and an activity measurement depends on: • the half-life of the radionuclide

- the measuring time
- the required sensitivity

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MEASURING RADIOACTIVITY

HOW TO ASSESS THE CONCENTRATION OF A CONTAMINANT IN A MATERIAL





HOW TO ASSESS THE CONCENTRATION OF A CONTAMINANT IN A MATERIAL

Sample C containing radioactive species R

Mass concentration

$$C_R = \frac{m_R}{m_C} \qquad \left[\frac{g}{g}\right]$$

$$A_{s} (^{232}Th) = 4.07 \times 10^{6} \left[\frac{Bq}{kg} \right]$$

$$a.i.=100\%$$

$$T_{1/2} (^{232}Th) = 1.40H$$

$$A_{s} (^{238}U) = 1.24 \times 10^{7} \left[\frac{Bq}{kg} \right]$$

$$\overline{\tau_{1/2} (^{238}U)} = 4.47E9$$

$$a.i.=99.28\%$$

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MEASURING RADIOACTIVITY









MASS CONCENTRATION ----- ACTIVITY

CONVERSIONS FOR THE NATURAL RADIOISOTOPES

232Th 1 [Bq/kg]
$$\leftrightarrow \frac{1}{4.07 \times 10^6}$$
 [g/g] = 24
238U 1 [Bq/kg] $\leftrightarrow \frac{1}{1.24 \times 10^7}$ [g/g] =
natK 1 [Bq/kg] $\leftrightarrow \frac{1}{3.18 \times 10^4}$ [g/g] = 31
40K 1 [Bq/kg] $\leftrightarrow \frac{1}{2.65 \times 10^8}$ [g/g] = 31

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1 [ppb] = 4.07 [mBq/kg]

1 [ppb] = 12.4 [mBq/kg]

 $1 \text{ [ppb]} = 31.8 \text{ [}\mu\text{Bq/kg]}$

1 [ppb] = 264.6 [mBq/kg]

- $10^{-6} \text{ g/g} = 1 \text{ ppm}$
- $10^{-9} \text{ g/g} = 1 \text{ ppb}$
- $10^{-12} \text{ g/g} = 1 \text{ ppt}$
- $10^{-15} \text{ g/g} = 1 \text{ ppq}$





CONCENTRATION OR ACTIVITY MEASUREMENT ?



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If secular equilibrium holds:

 $\lambda_1 N_1 = \lambda_2 N_2$

 $N_1 = \frac{\tau_1}{\tau_2} N_2$





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CONCENTRATION OR ACTIVITY MEASUREMENT ?



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If secular equilibrium holds:

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С

A





MOST POPULAR TECHNIQUES

U/TH SENSITIVITY COMPARISON

Technique	Application	U/Th sensitivity
Gamma Spectroscopy *	γ-emitters	10–100 μBq/kg
Alpha spectroscopy	210Po, α -emitters	< 1 µBq/cm²
Neutron Activation Analysis	decay chain progenitors	0.01 µBq/kg
Mass spectrometry	decay chain progenitors	0.01 µBq/kg
Liquid Scintillators	α, β emitting nuclides	1 mBq/kg
Radon emanation measurements	226Ra, 228Th	0.1–10 μBq/kg

*Only gamma spectroscopy can give info on secular equilibrium breaks!



EXAMPLE OF MEASUREMENT RESULTS: JUNO ACRYLIC SAMPLE

Sample:	Acrylic			
mass:	13.6 kg	Detect	or: GeMPI2, LNGS	
live time:	27 days	meas.	start: May 2021	
	Activity		Concentration	
Th-232:				
Ra-228	< 82 µBq/kg	\Leftrightarrow	< 2.0 E-11 g/g	
Th-228	< 95 µBq/kg	\Leftrightarrow	< 2.3 E-11 g/g	[Courtesv of M Lauber
U-238:				
Ra-226	< 47 µBq/kg	\Leftrightarrow	< 3.8 E-12 g/g	
Th-234	< 3.8 mBq/kg	\Leftrightarrow	< 3.1 E-10 g/g	
Pa-234m	< 0.67 mBq/kg	\Leftrightarrow	< 5.5 E-11 g/g	
U-235:	< 0.12 mBq/kg	\Leftrightarrow	< 2.1 E-10 g/g	R_{2} Ra 228 from A_{C} 228
К-40:	< 0.34 mBq/kg	\Leftrightarrow	< 1.1 E-8 g/g	Th-228 from Pb-212 & Bi-212 & T
Cs-137:	< 33 µBq/kg			U-235 from U-235 & Ra-226/Pb-2
Upper limits w	rith k=1.645. Uncertainties	are given	with k=1 (approx. 68% CL)







EXAMPLE OF MEASUREMENT RESULTS: CUORE COPPER SAMPLE

Sample:	le: OFE Copper						
mass:	7.64 kg	Detect	tor: GeMPI, LNGS				
live time:	37,5 days	meas.	start: January 2009				
	Activity		Concentration				
Th-232:				Pb-210:	< 1.4 Bq/kg		
Ra-228	< 0.12 mBq/kg	\Leftrightarrow	< 3.0 E-11 g/g	Co-60:	< 24 µBq/kg	@	start of
Th-228	< 64 µBq/kg	\Leftrightarrow	< 1.6 E-11 g/g	Co-57 :	(0.27 ± 0.13) mBq/kg	@	start of
U-238:				Co-58:	(32 ± 14) µBq/kg	@	start of
Ra-226	< 54 µBq/kg	⇔	< 4.3 E-12 g/g	Mn-54:	(64 ± 19) µBq/kg	@	start of
Pa-234m	< 3.3 mBq/kg	⇔	< 2.6 E-10 g/g				
U-235:	< 8.6 µBq/kg	⇔	< 1.5 E-10 g/g	Ra-228 from	n Ac-228	0	
К-40:	< 0.67 mBq/kg	⇔ < 2.2 E-8 g/g F		Ra-228 from	n Ra-226 & Pb-212 & H-20 n Ra-226 & Pb-214 & Bi-21	8	
Cs-137:	< 28 µBq/kg				n U-235 & Ra-226/Pb-214/I n Po-210	3i-124	
Upper limits with k=1.645. Uncertainties are given with k=1 (approx. 68% CL)				[Measured	by N	_ I. Laubens	

Monica







ÅBOVE GROUND LAB: COINCIDENCE CONFIGURATIONS TO INCREASE SENSITIVITY

	Copper	Acrylic
	5,4 kg	0,7 kg
Isotopo	MDA (mBq/kg)	MDA (mBq/kg)
²³² Th chain	< 3	< 10
²³⁸ U chain	< 2	< 4
⁴⁰ K	< 8	< 28
60 Co	< 1	< 3
137 C S	< 1	< 3

⁶⁰Co

Coincidenza HPGe-HPGe

⁶⁰Ni







ÅBOVE GROUND LAB: COINCIDENCE CONFIGURATIONS TO INCREASE SENSITIVITY

GeSpark

Table 3

MDA of the detector for the main nuclides in ²³⁸U, ²³⁵U and ²³²Th chains and ⁶⁰Co, all with a sample mass of 100 g and a measurement time of 31 d. The MDA expressed in g/g is relative to the parent nuclide of the chain assuming secular equilibrium.

Chain	Nuclide (decay)	E_{γ} (keV)	<i>€</i> ∙BR (%)	В	MDA (mBq/kg)	MDA (10 ⁻⁹ g/g)
	²²⁶ Ra (<i>a</i>)	186	0.126	0	8.0	0.64
²³⁸ U	²¹⁴ Pb (β)	352	0.804	137	26	2.1
	²¹⁴ Bi (β)	609	0.618	81	27	2.2
	²³⁵ U (<i>a</i>)	143.7	0.503	5	9.7	0.12
²³⁵ U	²¹¹ Bi (α)	351	0.286	2	12	0.15
	²¹¹ Pb (β)	405	0.074	102	252	3.2
	²²⁴ Ra (<i>a</i>)	241	0.108	0	9.4	2.3
²³² Th	$^{228}Ac (\beta)$	911	0.290	58	49	12
	208 Tl (β)	583	0.429	100	43	11
	⁶⁰ Co (β)	1173	0.843	40	14	$3.3 \cdot 10^{-10}$
		1332	0.757	38	15	$3.6 \cdot 10^{-10}$

Nuclear Inst. and Methods in Physics Research, A 1003 (2021) 165290

[Milano-Bicocca Radioactivity Lab]





PROS AND CONS FOR ULTRA-LOW BACKGROUND MATERIAL SCREENING

- Non destructive analysis
- No sample preparation required
- Sensitive to equilibrium breaking in the radioactive decay chains
- Very good detection sensitivities can be achieved
- Sizable sample masses are needed for high sensitivity
- Measuring times are long (~ several weeks) for high sensitivity
- Only sensitive to gamma emitters
- Accurate evaluation of the measurement efficiency is needed



Å POWERFUL TECHNIQUE FOR MASS CONCENTRATION MEASUREMENT

Neutron activation analysis (NAA) is a very sensitive method for qualitative and quantitative determination of elements based on the measurement of characteristic radiation from radionuclides formed directly or indirectly by neutron irradiation of the material.

• The principle is very simple:

 $A^{1+x} \rightarrow B+radiation$

- Multi-element capability
- Sensitivity for many elements













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BASIC PRINCIPLES



- A compound nucleus is formed (highly excited, unstable nucleus).
- The compound nucleus de-excites, usually by ejecting a small particle and a product nucleus.

The particle may be an elementary particle (neutron, electron, proton), an alpha particle or a photon. The product nucleus may be stable or radioactive.









Prompt radiation emitted ~10⁻¹² s after neutron capture.

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BASIC PRINCIPLES



- and a product nucleus.

 $_{Z\pm1}^{A+1}X$



Prompt gamma Analysis (PGA): measurement of γ rays during de-excitation of the compound nucleus after neutron capture





Commonly employed method in NAA. It is useful for many types of elements that produce radioactive nuclei. Measuring time and sensitivity depend on decay half-life.

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BASIC PRINCIPLES



- usually by ejecting a small particle and a product nucleus.

Delayed Gamma Neutron Activation Analysis (DGNAA): measurement of γ rays emitted during the decay of the product nucleus after the capture reaction is stopped.





NEUTRON SOURCE: NUCLEAR RESEARCH REACTORS

Owing to the high neutron flux, nuclear research reactors operating in the power region of 20 kW - 10 MW, with maximum thermal neutron fluxes of 10¹¹ – 10¹⁴ neutrons cm⁻² s⁻¹ are the most efficient neutron sources for high sensitivity activation analysis induced by epithermal and thermal neutrons.

Activation via (n, γ) reactions



Neutron capture cross section vs Energy for major actinides







Three key ingredients:

- High neutron flux
- High enough neutron capture cross section
- "Convenient" daughter nucleus (γ emission, half-life time)



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KEY INGREDIENTS

 ${}^{\mathsf{A}}\mathsf{X} + \mathsf{n} \longrightarrow {}^{\mathsf{A}+1}\mathsf{X} \longrightarrow {}^{A+1}_{Z+1}Y + \boldsymbol{\gamma}_{\text{cascade}}$

- Sensitivity depends on:
- type of material (short-lived activation products)
- neutron exposure time
- interferences in the matrix
- background in the region of the gamma emission

- care in the sample preparation is extremely important!
- the radiopurity of the sample container is also of concern!



NAA FOR 40K, 232TH, 238U

THE ACTIVATION REACTIONS







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- ⁴¹K isotopic abundance is 6.7%
- 40K isotopic abundance is 0.01%

⁴⁰K concentration is calculated from ⁴¹K one





NAA FOR 40K, 232TH, 238U

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ACTIVATION RATE

The number of radioisotopes that each second are created by neutron-induced reactions (the activation rate R) is related to the amount (N) of the original, stable (or long-lived) isotope in the sample:

 $R = \mathcal{N}$

At the end of the irradiation, the amount (N) of the original, stable isotope in the sample is calculated via the counts measured with HPGe detectors in the gamma peaks following the decays of the activated isotope:

$$n_{\rm dec} = \frac{R}{\lambda} \left(1 - e^{-\lambda t_{\rm irr}} \right) e^{-\lambda t_{\rm wait}} \left(1 - e^{-\lambda t_{\rm meas}} \right)$$

Usually irradiation standards are used, containing the same elements to be traced in the sample with a known amount, to be independent of the neutron flux and effective activation cross section.

$$\int \phi(E)\sigma(E) \mathrm{d}E$$



EXAMPLES OF ACHIEVABLE SENSITIVITIES







Acrylic samples

40

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Neutron irradiation:

TRIGA Mark II research reactor (250 kW) - Pavia, Italy

Contaminant concentration in an acrylic sample of 6 g

OK [ppt]	238U [ppt]	232Th [ppt]
)9 ± 0.02	< 0.17	< 0.13



EXAMPLES OF ACHIEVABLE SENSITIVITIES









Sample **mass is limited** at few tens of grams

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Neutron irradiation:

TRIGA Mark II research reactor (250 kW) - Pavia, Italy

LAB sample

Detector	LAB	Sample	²³⁸ U	²³² Th
	Sample	mass	[g/g]	[g/g]
β-Υ letector	Distillated	22g	<6·1E-14	<3·1E-13

Limit for the sentivity

Limit @ 90% C.L.

Presence of interferences ⁸²Br and ²⁴Na





HOW TO INCREASE THE SENSITIVITIES?



[Milano-Bicocca Radioactivity Lab]

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PMT











HOW TO INCREASE THE SENSITIVITIES?

Extraction Chromatography

Column Chromatography



The stationary phase: column and actinide absorb resin (TRU or TEVA)

The mobile phase or eluent is a solvent used to move the compounds through the column.

Ideally the column chromatography selectively absorbs actinide activities (U, Th, Pa ,Np) while allowing interferences (Br, Na) pass through





PROCEDURE DEVELOPED AT MILANO-BICOCCA FOR THE JUNO LIQUID SCINTILLATOR



Chemical/Radiochemical Treatments (Pre and Post Irradiation)



Allow to remove interferences and concentrate the sample



Allows to transform long life nuclides ²³⁸U/²³²Th into the radioactive short life ²³⁹Np/²³³Pa nuclides. Sensitivity < 1ppt



We developed a new detector suitable for $\beta - \gamma$ coincidence measurements of irradiated liquid samples

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Any sample manipulation before neutron irradiation could introduce contaminations (radiopurity of containers is also crucial)





 $^{232}_{90}Th + n \longrightarrow ^{233}_{91}Pa$ $^{238}_{92}U + n \longrightarrow ^{239}_{93}Np$









PROCEDURE DEVELOPED AT MILANO-BICOCCA FOR THE JUNO LIQUID SCINTILLATOR

Our to-date best achievements for natural contaminants in JUNO LS

Nuclide	Sensitivity @ 95 %	Limitating factor
238U	< 0,7 ppq @ 500 mL < 0,4 ppq @ 1 L	Resin background
232 Th	< 1,6 ppq @ 1 L	Activation rate and resin background
40 K	<0,7 ppq @ 126 g	Sample mass, interfering element (Na) and high contamination probability



HOW TO INCREASE THE SENSITIVITIES?



 $\beta - \gamma$ coincidence detector: GeSparK

> Beta-gamma coincidence ²³⁹Np delayed coincidence

Radiochemical treatments

- Concentration of the nuclides of interest (higher equivalent sample mass)
- Removal of interfering nuclides







PROS AND CONS FOR ULTRA-LOW BACKGROUND MATERIAL SCREENING

- High Sensitivity: NAA can detect trace amounts of natural contaminants with sub-ppt sensitivities.
- Non-Destructive: the sample remains mostly intact after analysis.
- After the neutron irradiation, samples can be further treated (e.g. radiochemistry) without the risk of contamination.
- Small samples are required.
- Only sensitive to decay chain precursors
- Not effective for all elements
- Measuring times are long for U/Th (up to 4 weeks for Th)



INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY

ICP-MS, **INORGANIC MASS SPECTROMETRY**







INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY

THE ION SOURCE



Plasma torch ion source

<u>Plasma is capable to ionize almost all</u> chemical elements











MEASURABLE ELEMENTS

H		_								
Li	Be									
Na	Mg			_						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	C
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	A
Cs	Ba	La	Hf	Ta	w	Re	Os	Ir	Pt	A
Fr	Ra	Ac								

Ce	Pr	Nd	Pm	Sm	Eu	G
Th	Pa	U	Np	Pu	Am	C

Ultra - trace

[credits: S. Nisi]

1ppq (10⁻¹⁵ g/g)

1ppt (10⁻¹² g/g)

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THE MAGNETIC SECTOR



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QUADRUPOLE MASS ANALYSER



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RECENT ADVANCES IN QUADRUPOLE MASS ANALYSER



He gas collision cell

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[credits: S. Nisi]

ICP-MS

Triple quadrupole



THE ELECTROSTATIC SECTOR

• Circular trajectory: centripetal force equals the electrostatic force



- No mass dispersion

ICP-MS

• With the slit at a particular radius, the systems acts as an energy filter



DOUBLE FOCUSING MASS SPECTROMETER



[credits: S. Nisi]

ICP-MS



Element 2 @ LNGS

Double focusing ICP-MS have high sensitivity and high mass resolution





ICP-MS

WHAT IS NEEDED FOR HIGH SENSITIVITY MEASUREMENTS





Sample preparation



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[credits: S. Nisi]

Instrumentation





"Clean chemistry"





EXAMPLE OF MEASUREMENT RESULTS: COPPER SAMPLE

	Measured in Cu sample		DL* (in solid Cu
Th	4.6 ± 1.3 ppt	Th	2.6 ppt
U	1.0 ± 0.3 ppt	U	0.8 ppt

*DL = 3 × BLKStdDev

[Measured by S. Nisi]





EXAMPLE OF MEASUREMENT RESULTS: ROMAN LEAD SAMPLE

	Conc [10 ⁻¹² g/g]	[µBq/Kg]
Th232	1,2 ± 0,6	4,9 ± 2,5
U238	1,2 ± 0,5	15 ± 7

	Method Detection Limit* [10 ⁻¹² g/g]
Th232	0,5
U238	0,3

[Measured by S. Nisi]

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Roman Pb contaminations

*DL = 3 × BLKStdDev


EXAMPLE OF MEASUREMENT RESULTS: TEFLON (PTFE) SAMPLE

Contaminations in PTFE samples						
Element	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Th	[pg*g-1]	9.9 ± 3.0	7.4 ± 2.2	< 10	3.4 ± 1.0	2.0 ± 0.6
U	[pg*g-1]	14.8 ± 4.4	13.3 ± 4.0	< 10	8.2 ± 2.5	0.8 ± 0.2
K	[ng*g-1]	32.3 ± 9.7	34.3 ± 10.3	< 20	< 10	< 20

[Measured by S. Nisi]

ICP-MS



LASER ABLATION ICP-MS

AN INTERESTING RECENT DEVELOPMENT TO SCREEN SOLID SAMPLES



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LASER ABLATION ICP-MS

APPLIED TO JUNO ACRYLIC SAMPLES

- A very interesting method to assess the surface radiopurity of a solid material
- Caveat: surface impurities may not be uniformly distributed on the sample
- The bottleneck with this method is the quantification of U/Th contamination level

Acrylic sample 25 mm 25 mm 2D scan of a square of 600x600 µm² with a laser spot of 8 µm Laser scans Acrylic 600 µm Several 2D laser scans to explore the Z-axis 3D profile measurement scan 4 µm depth SUMACO

2 scans

8 µm depth

[credits: F. Perrot]





ICP-MS

PROS AND CONS FOR ULTRA-LOW BACKGROUND MATERIAL SCREENING

- Sensitivity: Can detect elements at extremely low concentrations (ppt or even lower). • Very fast analysis: high sensitivity measurement can be performed in a few hours. • Small sample masses are needed: best technique to check different material batches. Wide dynamic range: Can measure concentrations over several orders of magnitude. • • Multi-element detection: Simultaneously detects multiple elements in a single run.

- Destructive analysis and high risk of contamination during sample preparation and measurement.
- Interference: ICP-MS can suffer from spectral interferences. This can be mitigated by using techniques like collision/reaction cells.
- Matrix effects: The presence of high concentrations of other substances in the sample can affect the ionization efficiency or cause signal suppression.
- Low sensitivity for ⁴⁰K.





WHAT WE HAVE SEEN UNTIL NOW

- Material screening for ultra-low background experiments is **highly challenging** and often requires dedicated R&D to achieve the necessary sensitivities.
- Gamma spectroscopy with HPGe detectors is the most effective method for providing comprehensive information on both natural contaminants (including entire decay chains) and anthropogenic radionuclides in a single measurement. In the best detector configurations, sensitivities can reach the low tens of ppt, though extended measurement times are often required.
- NAA and ICP-MS offer even higher sensitivities, reaching sub-ppt levels, but are limited to detecting natural decay chain progenitors.
- These techniques are **complementary**: gamma spectroscopy provides broad coverage, while NAA and ICP-MS deliver deeper sensitivity for specific elements.

A SHORT SUMMARY



IS MATERIAL SCREENING ALL WE NEED?

THIS IS NOT THE END OF THE STORY

Once a material that meets our requirements has been identified, several factors still require careful consideration:

- Material consistency: different batches may vary in quality. It is crucial to same production batch that was screened.
- contaminants, both natural and artificial. We must oversee the entire into contact with our sample.
- Storage conditions: proper storage is essential to prevent surface recontamination, such as radon plate-out.
- requiring extra precautions.

coordinate with the vendor to ensure that the entire quantity comes from the

• Machining contamination: the machining process can introduce unwanted production chain and consider additional screenings for all materials that come

• Surface cleanliness: the surface of the material may not be as clean as the bulk,



THE METHOD TO SCREEN SURFACES

- In same cases those contaminations can become the ultimate limitation to sensitivity (e.g. CUORE experiment)

CUORE: 2039 kg×y of TeO₂ exposure [arXiv 2404.04453]



contaminations on surfaces

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• Surface contaminations are a great concern for $0\nu\beta\beta$ and dark matter searches

• Unfortunately, at present, only few technologies are able to measure low levels



WITH COMMERCIAL DETECTORS FOR SMALL SAMPLES

- Si barrier detectors with 900 mm² active area
- Sample size: 5×5 cm²
- Typical sensitivity for U/Th chains: ~ μBq/cm²
- Typical measuring time: ~ 30 days





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[Milano-Bicocca Radioactivity Lab]







WITH COMMERCIAL DETECTORS FOR LARGE SAMPLES

- XIA Ultralo 1800 Alpha counter (https://xia.com)
- Sample size: 43×43 cm²
- Sensitivity for ²¹⁰Po: ~ 10 nBq/cm²
- Measuring time: ~76 days

[Credits: G. Zuzel, LRT 2022]



WITH AN AD-HOC DETECTOR: THE BI-PO3 DETECTOR AT LSC

- Sample size: 3.6 m^2
- Sensitivity for ${}^{208}\text{Tl}/{}^{214}\text{Bi:} \sim 0.1 \text{ nBq/cm}^2$
- Measuring time: ~76 days





[Credits: P. Loaiza]



WHAT IF YOU NEED MORE?

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BUILDING YOUR OWN "CUSTOM" DETECTOR

EXAMPLE: CUORE CRYSTAL VALIDATION RUNS (CCVR)

- control of the mass production of the detector material



CUORE detector module



Upper limits at 90% C.L. on the activity and on the bulk contamination of uranium and thorium decay chains in the hypothesis of secular equilibrium.

Chain	Nuclide	Upper limit [Bq/kg]	Upper limit [g/g]
²³⁸ U	²³⁸ U	2.5E-07	2.0E-14
	²³⁴ U	4.7E-07	3.6E-14
	²³⁰ Th	5.7E-07	4.4E-14
	²²⁶ Ra	6.7E-07	5.3E-14
	²¹⁸ Po	1.6E-07	1.3E-14
²³² Th	²³² Th	1.3E-07	3.1E-14
	²¹² Bi	8.4E-07	2.1E-13

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In some cases, "standard" techniques do not reach the required sensitivity.

• You may need to develop an ad-hoc experimental setup, e.g. for the periodic

Upper limits at 90% C.L. for surface contamination, for different penetration length values. See text for details on the calculation of confidence intervals.

Depth	Nuclide	Upper limit 90% C.L
0.01 μm	²³⁸ U	3.1E-09
	²²⁶ Ra	6.3E-09
	²³² Th	1.6E-09
0.1 μm	²³⁸ U	3.2E-09
	²²⁶ Ra	6.6E-09
	²³² Th	1.6E-09
0.2 μm	²³⁸ U	3.8E-09
	²²⁶ Ra	7.6E-09
	²³² Th	2.0E-09
1 <i>µ</i> m	²³⁸ U	3.7E-09
	²²⁶ Ra	8.9E-09
	²³² Th	1.9E-09
5 <i>µ</i> m	²³⁸ U	2.0E-09
	²²⁶ Ra	5.4E-09
	²³² Th	1.0E-09
10 µm	²³⁸ U	1.7E-09
-	²²⁶ Ra	4.4E-09
	²³² Th	8.3E-10

[Astroparticle Physics 35 (2012) 839–849]











[2016 JINST 11 P07009]



EXAMPLE: CUORE-O, THE FIRST CUORE TOWER

Table 8 List of the sources used to fit the CUORE-0 background data.
 The columns show (1) the name of the contaminated element, (2) the source index (j in Eq. 1), and (3) the contaminant. If not otherwise specified, ²³²Th, ²³⁸U, and ²¹⁰Pb refer to the whole decay chains in secular equilibrium, while the label "only" indicates that only the decay of the specified isotope is generated. For surface contaminants, the simulated

depth is indicated in μ m. Column (4) reports the prior used in the fit, when not specified a non-informative prior is used (see text for details). Column (5) reports the posterior with the statistical error (limits are 90% C.L.). Column (6) reports the range of systematic uncertainties (limits are 90% C.L.). In the case of crystal sources, systematic uncertainties can arise from non-uniform contaminants in the different crystals

1 1	0				•		40
Component	Index	Bulk sources	Prior [Bq/kg]	Posterior [Bq/kg]	Systematics [Bq/kg]		41
Crystals	1	130 Te – $2\nu\beta\beta$		$3.43(9) \times 10^{-5}$	$3.1 \times 10^{-5} - 3.7 \times 10^{-5}$		42
	2	²¹⁰ Po	$2.36(11) \times 10^{-6}$	$2.39(11) \times 10^{-6}$			44
	3	²¹⁰ Pb		$1.37(19) \times 10^{-6}$	$5.4 \times 10^{-7} - 2.2 \times 10^{-6}$		45
	4	²³² Th (only)		$7(3) \times 10^{-8}$	$< 1.2 \times 10^{-7}$		40
	5	²²⁸ Ra– ²⁰⁸ Pb		$< 3.5 \times 10^{-8}$	$< 7.5 \times 10^{-8}$		47
	6	238 U $^{-230}$ Th		$< 7.5 \times 10^{-9}$	$< 3.6 \times 10^{-8}$		Holder 48
	7	230 Th(only)		$2.8(3) \times 10^{-7}$			49
	8	²²⁶ Ra– ²¹⁰ Pb		$< 7.0 \times 10^{-9}$	$< 2.2 \times 10^{-8}$		51
	9	⁴⁰ K		$5.1(14) \times 10^{-6}$	$< 8.2 \times 10^{-6}$		52
	10	⁶⁰ Co	$< 3.0 \times 10^{-7}$	$< 5.1 \times 10^{-7}$			CryoInt 53
	11	¹²⁵ Sb		$9.6(4) \times 10^{-6}$	$7.5 \times 10^{-6} - 1.2 \times 10^{-5}$		IntPb 54
	12	¹⁹⁰ Pt		$2.00(5) \times 10^{-6}$	$1.6 \times 10^{-6} - 2.3 \times 10^{-6}$		Component
Holder	13	²³² Th	$< 2.0 \times 10^{-6}$	$< 2.1 \times 10^{-6}$			50 m K Sm of 55
	14	²³⁸ U	$< 6.5 \times 10^{-5}$	$< 1.2 \times 10^{-5}$	$< 2.2 \times 10^{-5}$		Bottom plate ExtPh 56
	15	⁴⁰ K	$7(2) \times 10^{-4}$	$8(2) \times 10^{-4}$		1.01	Bonom plate EMI 0 50
	16	⁶⁰ Co	$5(1) \times 10^{-5}$	$3.5(8) \times 10^{-5}$		$ > 10^{4} \equiv$	
	17	⁵⁴ Mn		$1.0(2) \times 10^{-5}$	$< 1.7 \times 10^{-5}$	E E	
	18	⁵⁷ Co		$2.9(3) \times 10^{-5}$	$2.3 \times 10^{-5} - 3.7 \times 10^{-5}$		
CryoInt	19	²³² Th		$< 1.5 \times 10^{-5}$	$< 3.5 \times 10^{-5}$	× 103	
	20	²³⁸ U		$< 1.5 \times 10^{-5}$	$< 3.9 \times 10^{-5}$		1
	21	⁴⁰ K		$1.1(3) \times 10^{-3}$		n, ■-	where here is a second second
	22	⁶⁰ Co	$< 1.8 \times 10^{-4}$	$2.4(10) \times 10^{-5}$			and have a second when the
	23	¹³⁷ Cs		$9.9(15) \times 10^{-6}$		10^{2}	
IntPb	24	²³² Th	$< 4.5 \times 10^{-5}$	$5.3(7) \times 10^{-5}$	$1.7 \times 10^{-5} 6.6 \times 10^{-5}$		
	25	²³⁸ U	$< 4.6 \times 10^{-5}$	$2.7(10) \times 10^{-5}$		E E	
	26	⁴⁰ K	$< 2.3 \times 10^{-5}$	$<2.4 \times 10^{-5}$	$< 4.6 \times 10^{-4}$		
	27	108m Ag		$6.1(12) \times 10^{-6}$		10	
	28	²⁰² Pb		$6(3) \times 10^{-6}$		1 1	
CryoExt	29	²³² Th		$< 1.2 \times 10^{-4}$	$< 1.8 \times 10^{-4}$		
	30	²³⁸ U		$2.4(6) \times 10^{-4}$	$< 5.9 \times 10^{-4}$		
	31	40 K		$< 1.6 \times 10^{-3}$	$< 2.6 \times 10^{-3}$	1 =	
	32	⁶⁰ Co	$< 4.2 \times 10^{-5}$	$2.5(9) \times 10^{-5}$			
ExtPb	33	²³² Th	$< 2.6 \times 10^{-4}$	$3.1(3) \times 10^{-4}$	$2.1 \times 10^{-4} - 3.5 \times 10^{-4}$		
	34	²³⁸ U	$< 7.0 \times 10^{-4}$	$5.0(6) \times 10^{-4}$	3.5×10^{-4} - 6.2×10^{-4}		
	35	⁴⁰ K	$< 5.4 \times 10^{-3}$	$3.1(5) \times 10^{-3}$		10 ⁻¹	
	36	²⁰⁷ Bi		$5.9(5) \times 10^{-5}$	$4.7 \times 10^{-5} 7.2 \times 10^{-5}$		500
	37	²¹⁰ Pb		5.96(11)	5.4-6.3		

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BUILDING A PROTOTYPE



1000

1500

2000

[Eur. Phys. J. C (2017) 77:13]



85

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