Production of ^{236}Pu of Suitable Purity as a Chemical Yield Tracer for Environmental Analysis

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Plutonium-236

- Why do we need it
- How we make it
- Recent work at NPL and Birmingham
- Future work

Plutonium analysis

- Several methods available

  Gravimetric

  Titrimetric

  γ spectrometry

  α spectrometry

  Mass spectrometry

  Mass and α spectrometry need yield monitor

Yield monitors/tracers

- What makes a good tracer?

Chemical behaviour is the same as the analyte throughout the analysis

Chemical equilibrium between tracer and sample established as soon as possible in the analysis

Tracer and analyte can be determined in each other’s presence with suitable accuracy

Harvey, B.R. and Lovett, M.B., *Nuclear Instruments and Methods*, 223, 224-234, (1984)

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Plutonium yield tracers

- Several options exist

^{236}Pu – α emitter, suitable for α spectrometry
^{237}Pu* – β emitter, possible for α and mass spectrometry
^{238}Pu – α emitter, not suitable – present in nuclear fuel
^{239}Pu – α emitter, not suitable – present in nuclear fuel
^{240}Pu – α emitter, not suitable – present in nuclear fuel
^{241}Pu – α emitter, not suitable – present in nuclear fuel
^{242}Pu - α emitter, suitable for α and mass spectrometry
^{244}Pu - α emitter, suitable for α and mass spectrometry

* Only if separate measurement made

Likely nuclides

- Four choices

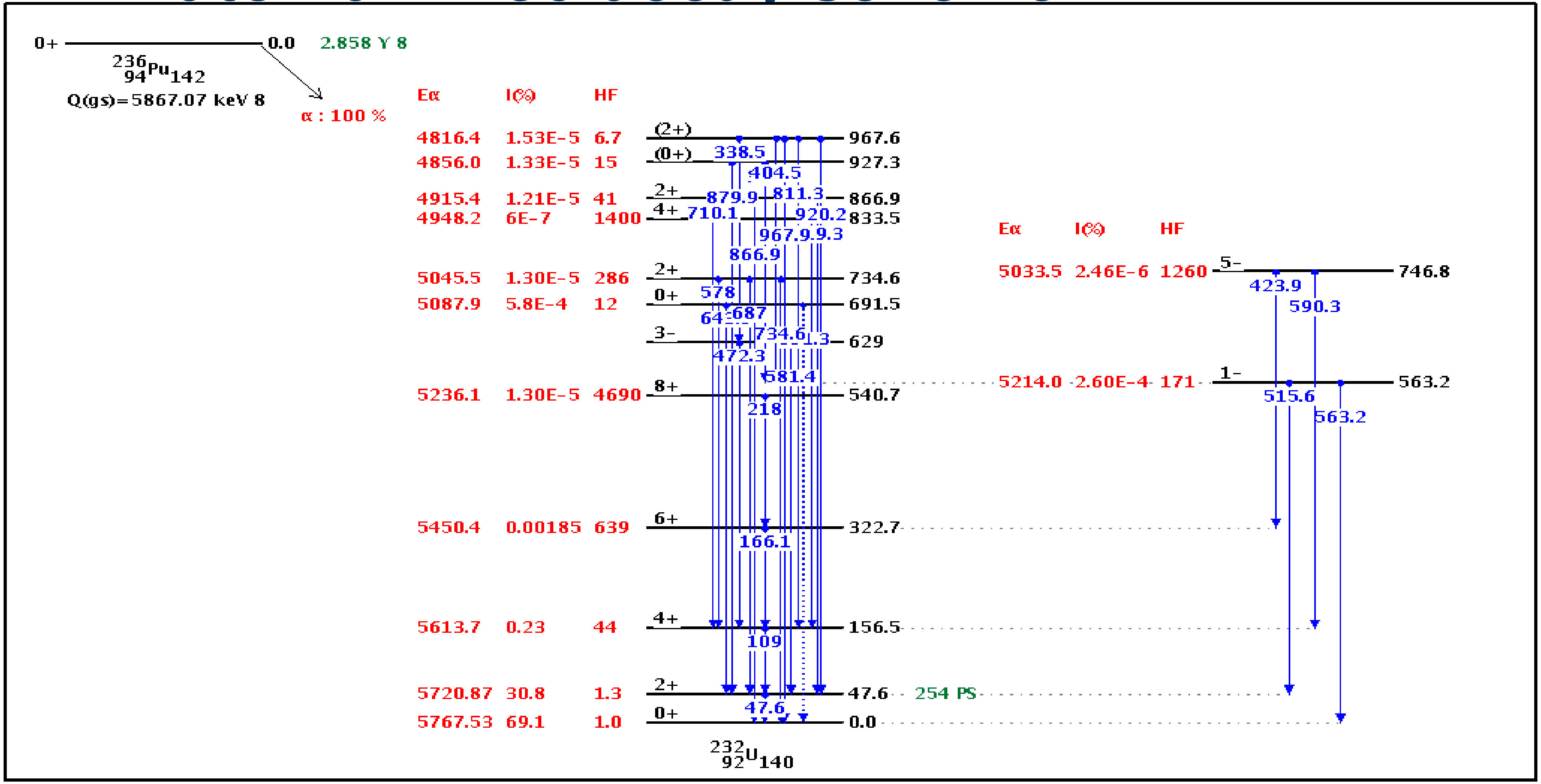
^{236}Pu – Short half life (1044 days); decays to ^{232}U, ^{228}Th et seq; purity may be an issue; intermittently available

^{237}Pu – Short half life (45 days); decays to ^{237}Np; no availability

^{242}Pu - Long half life (3.73×10^{5} years); daughters not an issue; low levels in nuclear fuel; supplies running out of suitably pure material

^{244}Pu - Long half life (8.0×10^{7} years); daughters not an issue; purity good only for mass spectrometry; availability is reasonable

Plutonium-236 decay scheme



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Plutonium-236 decay radiation

α decay – 100% (spontaneous fission < 1×10^{-6}%):

5721.00 (± 0.10) keV, intensity 30.56 (± 0.45)%

5767.66 (± 0.08) keV, intensity 69.26 (± 0.45)%

X-rays:

11.62 keV, intensity 0.28 (± 0.03)%

~13.5 keV, intensity ~4.6 (± 0.3)%

15.40 keV, intensity 0.113 (± 0.011)%

16.41 keV, intensity 1.07 (± 0.07)%

~17.1 keV, intensity ~4.5 (± 0.4)%

~20.5 keV, intensity 1.2 (± 0.2)%

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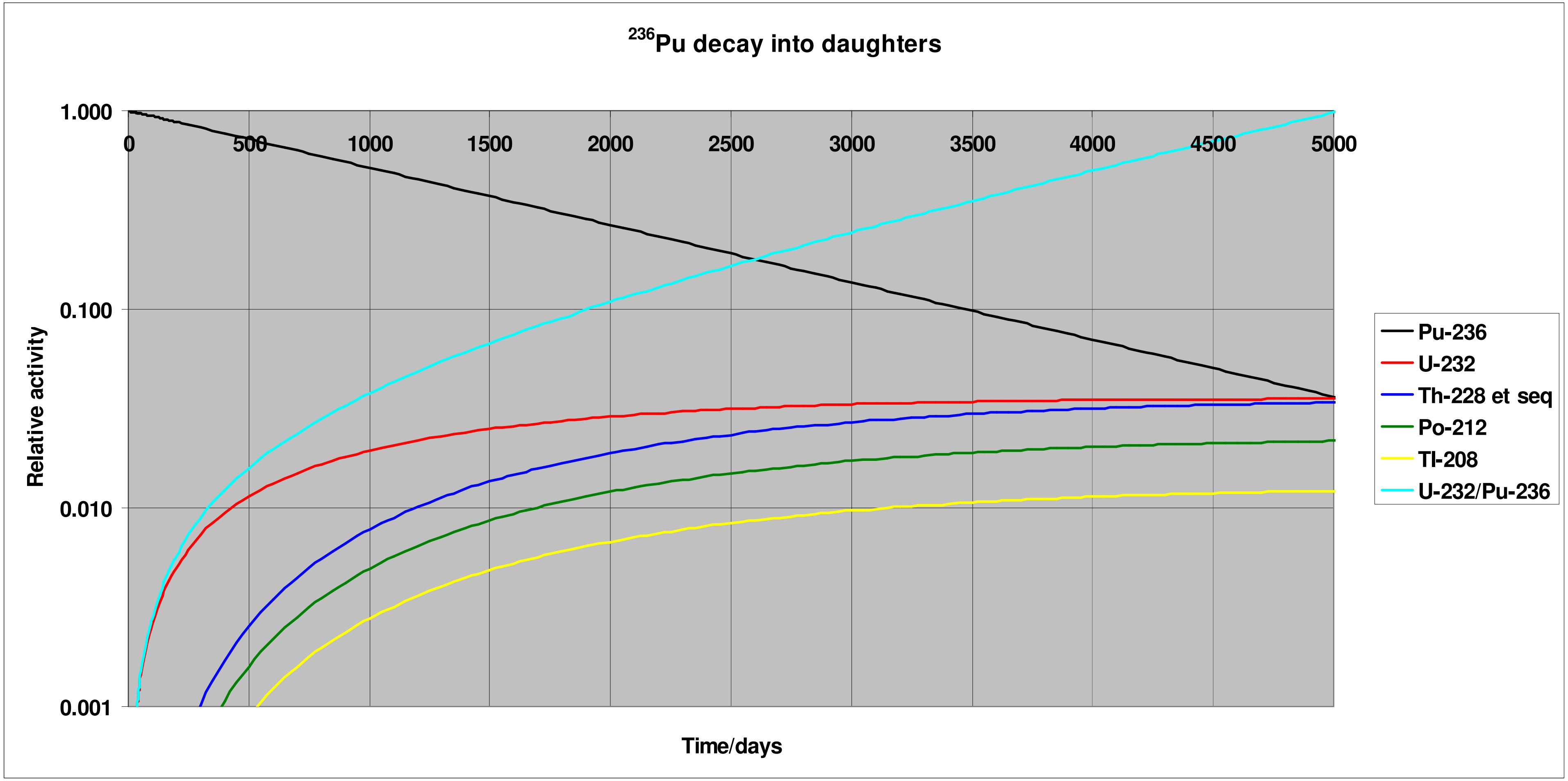
Plutonium-236 daughter radionuclides



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Production

- Different routes available

  Buy it!

  Which we did – and produced a batch of low level (5g @ 10 Bq/g) and high level standards (5g @ 150 Bq/g) – contact Chris Gilligan: chris.gilligan@npl.co.uk

  Charged particle irradiation of Uranium

  Photon irradiation of ^{237}Np

  Decay of ^{236m}Np

  Purity is the issue

Charged particle irradiation

- Various possibilities – but mainly
  - Irradiation of ^{235}U with α particles at up to 40 MeV
    - ^{236}Pu, ^{237}Pu and ^{238}Pu produced directly and ^{236}Pu and ^{238}Pu produced from β decay of ^{236m}Np and ^{238}Np; also ^{239}Pu and ^{240}Pu from ^{238}U; fission products
  - Irradiation of ^{238}U with protons at up to 50 MeV
    - ^{236}Pu and ^{238}Pu produced from β decay of ^{236m}Np and ^{238}Np; also ^{235}Np and ^{237}Np; fission products
  - Irradiation of ^{235}U with deuterons below 20 MeV
    - ^{235}Np produced directly; ^{236}Pu produced from β decay of ^{236m}Np; also ^{238}Pu from ^{237}Np, ^{239}Pu and ^{240}Pu from ^{238}U; fission products

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Irradiation of ^{235}U with deuterons

- Selected as route with best potential for purity

$^{235}U(d,2n)^{235}Np$	Useful
$^{235}U(d,n)^{236m}Np(\beta^{-},48\%)^{236}Pu$	**Required**
$^{235}U(d,n)^{236m}Np(\varepsilon,52\%)^{236}U$	Not an issue
$^{235}U(d,n)^{236g}Np$	Useful
$^{238}U(d,2n)^{238}Np(\beta^{-})^{238}Pu$	*Problem*
$^{238}U(n,\gamma)^{239}Np(\beta^{-})^{239}Pu$	*Problem*
$^{237}Np(d,n)^{238}Pu$	*Problem*
$^{237}Np(n,\gamma)^{238}Np(\beta^{-})^{238}Pu$	*Problem*
$^{238}Pu(n,\gamma)^{239}Pu(n,\gamma)^{240}Pu$ &c	*Problem*

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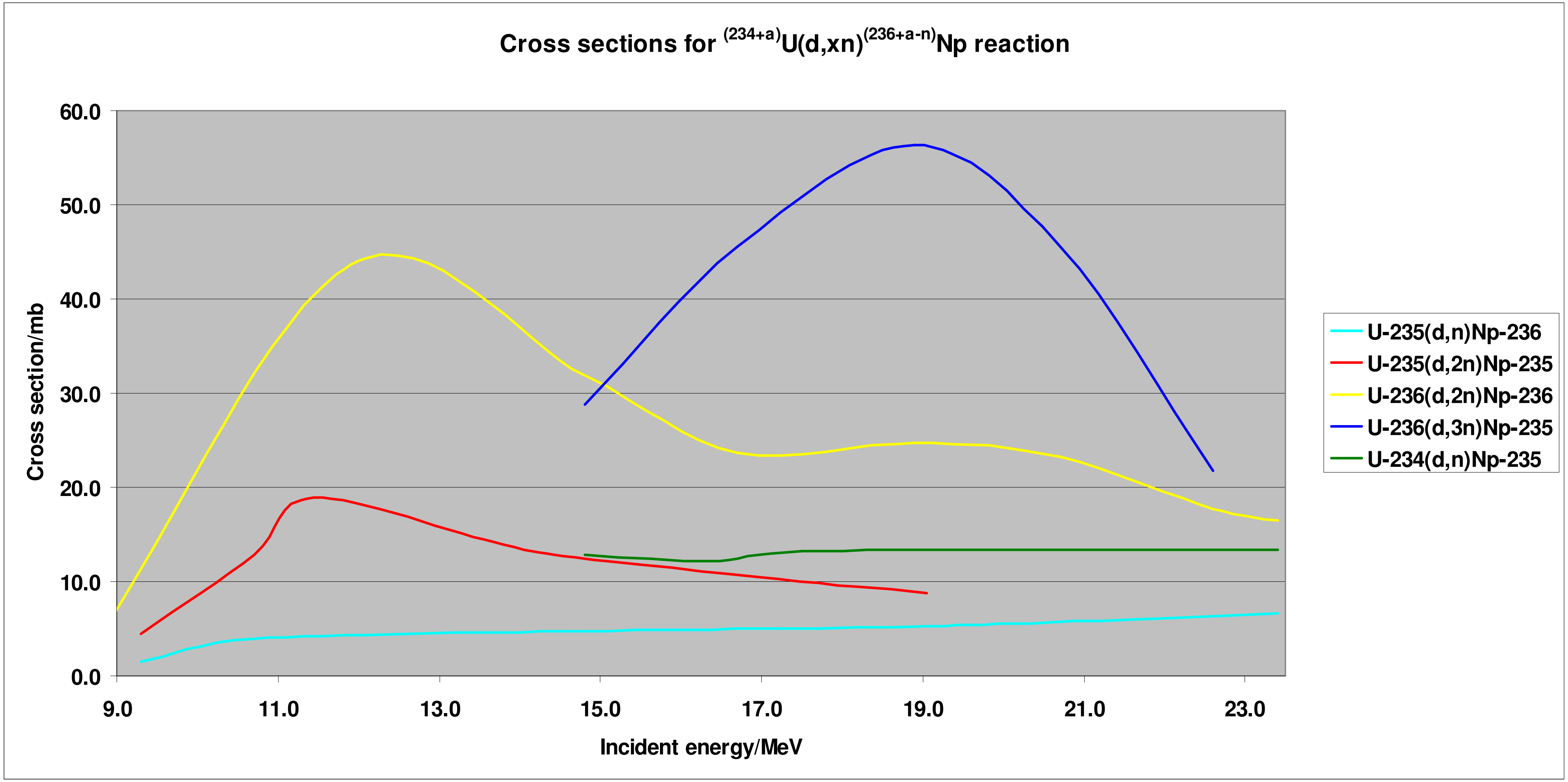
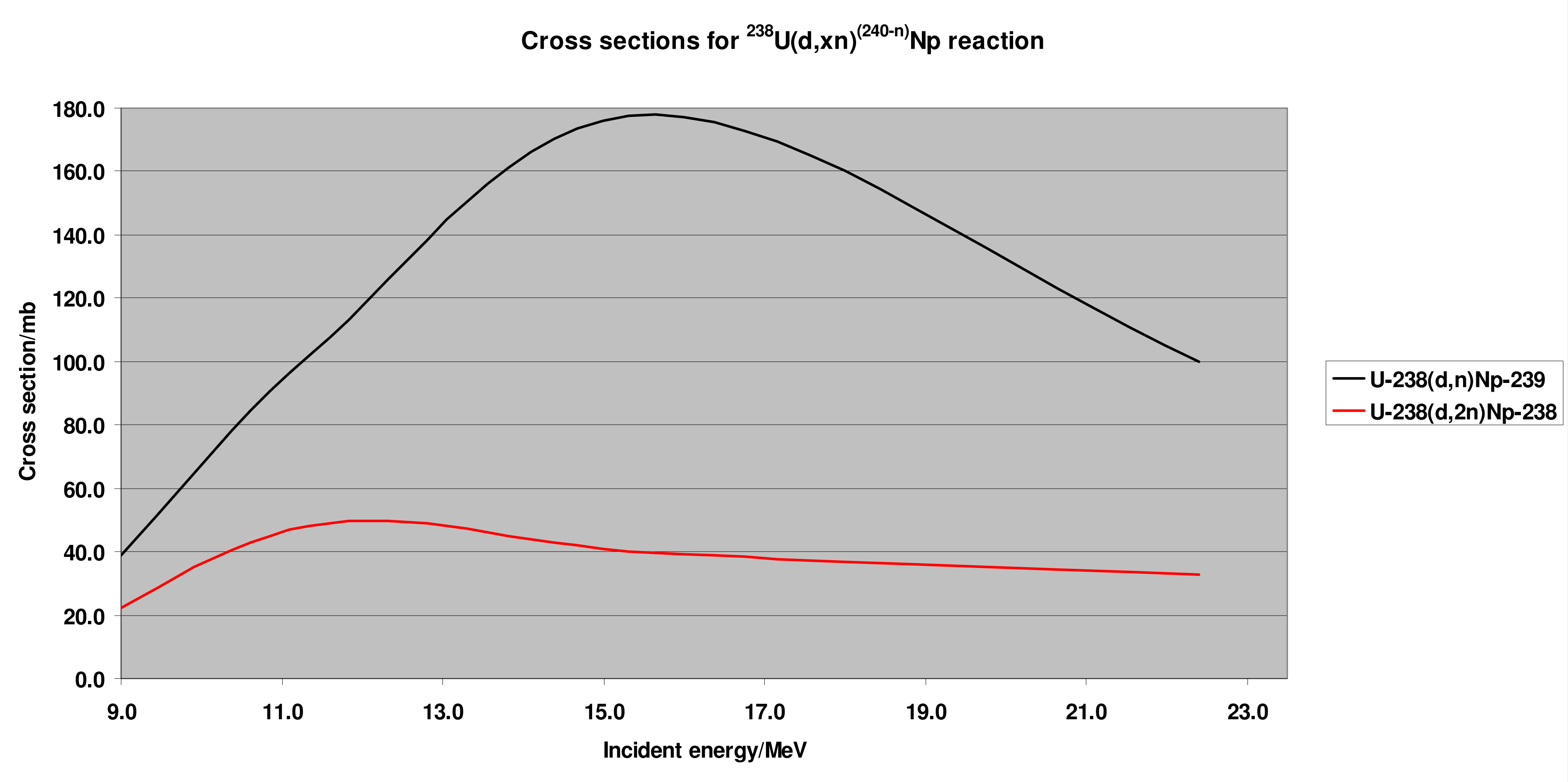
Irradiation of ^{235}U and ^{236}U with deuterons



Irradiation of ^{238}U with deuterons



Irradiation of ^{235}U with Deuterons (1990)

- Products

^{233}Np: From ^{233}U(d,2n), not important

^{234}Np: From ^{233}U(d,n) and ^{234}U(d,2n), not important

^{235}Np: From ^{234}U(d,n) and ^{235}U(d,2n), important

$^{236m/g}$Np: From ^{235}U(d,n) and ^{236}U(d,2n), important

^{237}Np: From ^{236}U(d,n), not (very) important

^{238}Np: From ^{238}U(d,2n), important – impurity; leading to ^{238}Pu

^{239}Np: From ^{238}U(d,n), important – impurity; leading to ^{239}Pu

Irradiation of ^{235}U with Deuterons (1990)

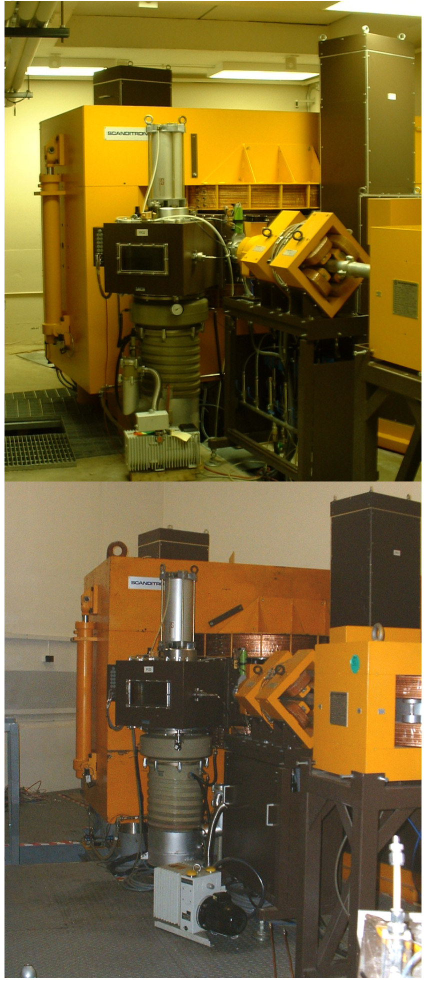
- Results obtained by Efurd

^{235}Np – ~7.4 MBq (~3.7×10^{14} atoms)
^{236m}Np – ~1.7 GBq (~2×10^{14} atoms)
^{236g}Np – ~8.5 Bq (~6×10^{13} atoms)
^{237}Np – ~0.13 Bq (~1.3×10^{13} atoms)

^{236}Pu – ~1.5 MBq (~2×10^{14} atoms from ^{236m}Np decay) – ~190 Bq/g/µA/h
^{238}Pu – ~820 Bq (~3.3×10^{12} atoms)
^{239}Pu – ~12 Bq (~1.3×10^{13} atoms)
^{240}Pu – ~0.051 Bq (~1.5×10^{10} atoms)

…and 8×10^{16} fissions

University of Birmingham Cyclotron



- Scanditronix MC40 cyclotron transferred from Minneapolis to Birmingham in 2002-2004
  - Proton beam: <9 and 12 – 39 MeV
  - Deuteron beam: 6 – 19.5 MeV
  - ^{3}He beam: <27 and 36 – 54 MeV
  - α beam: 12 – 39 MeV
  - 12-way switching magnet added in 2005 (ex Strasbourg)
  - Extended to second target room (with original switching magnet) in 2007

University of Birmingham Cyclotron

- Main work is isotope production:
  - ^{81}Rb (^{82}Kr(p,2n) at 30 MeV) 75 GBq per night, 5 nights per week - two dedicated target stations
  - ^{18}F and other positron emitters for industrial PET research
  - Thin layer activation
    - Conventional p and d activations
    - ^{3}He activation of diamond-like carbon
    - UTLA activation of plastics ^{12}C(^{3}He, 2α)^{7}Be
  - Radiation effects (very low currents)
  - Local facility for nuclear physics

Irradiation of ^{235}U with Deuterons (2009)

- Irradiation at Birmingham, chemistry at NPL

^{235}U enrichment:	99.887% (^{233}U – <0.0005%, ^{234}U – 0.034%, ^{236}U – <0.025**%,** **^{238}U – <0.053%**)
Amount irradiated:	0.08 grams
Incident energy:	19 MeV
Target thickness:	~25 mg/cm^2
Irradiation time:	2 hours
Target backing:	Copper

Irradiation of ^{235}U with Deuterons (2009)

- Chemistry at NPL

  Precipitation of actinides with yttrium
  Dissolve $Y(OH)_3$ in HCl
  Anion exchange in 6M HCl
    Uranium, Neptunium and Plutonium retained by resin
  Wash column with 12M HCl
  Remove Plutonium with 12M HCl/0.1M NH_4I
  Remove Neptunium with 3M HCl
  Recover Uranium with 0.1 M HCl
  Repeat clean up on actinide fractions

Irradiation of ^{235}U with Deuterons (2009)

- Results obtained in 2009

^{235}Np – ~7.4 kBq (~3.7×10^{11} atoms)

^{236m}Np – ~1.7 MBq (~2×10^{11} atoms)

^{236g}Np – ~0.0085 Bq (~6×10^{10} atoms)

^{237}Np – ~0.00013 Bq (~1.3×10^{10} atoms)

^{236}Pu – ~1.5 kBq (~2×10^{11} atoms from ^{236m}Np decay) – ~310 Bq/g/µA/h

^{238}Pu – <6 Bq (<2.4×10^{10} atoms)

^{239}Pu – <2.1 Bq (<2.3×10^{12} atoms)

^{240}Pu – <2.1 Bq (<6.3×10^{11} atoms)

500 MBq ^{65}Zn…

…and 4.5×10^{13} fissions

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Irradiation of ^{235}U with Deuterons (2009)

- Results obtained in 2009

^{236}Pu – >99.5% by activity

^{238}Pu – <0.38% by activity*

^{239}Pu – <0.14% by activity*

^{240}Pu – <0.14% by activity*

Overall yield better

Need to improve purity assay

Repeat experiment by end of year with thicker target

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* - upper limit

Irradiation of ^{235}U with Deuterons (2009)

- Results obtained in 2009

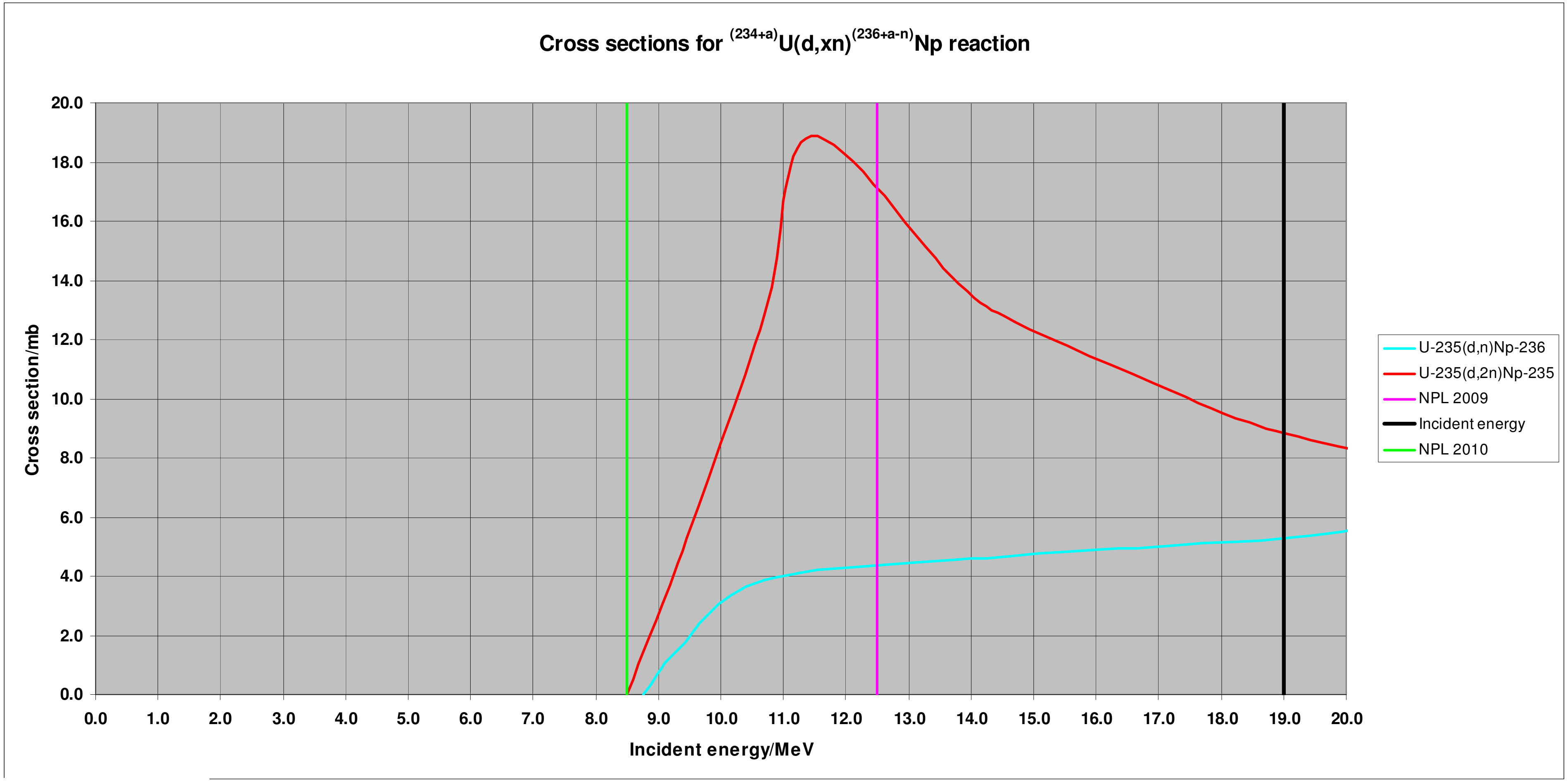
  Yield (as Bq/g/µA/h) better as

  – less wasted on purely fission reaction (<8.5 MeV)

  – Expect lower neutron yield, so fewer ^{238}U(n,γ)^{239}Np(β^{-})^{239}Pu reactions

  – Lower fission yield, so easier to handle

Irradiation of ^{235}U with Deuterons



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Irradiation of ^{235}U with Deuterons (2009)

- Next irradiation

  ^{235}U enrichment: 99.887%

  (^{233}U – <0.0005%, ^{234}U – 0.034%,
  ^{236}U – <0.025**%, ^{238}U – <0.053%**)

  Amount irradiated: 1.2 grams

  Incident energy: 19 MeV

  Target thickness: ~380 mg/cm^2

  Irradiation time: 20 hours

  Target backing: Copper

Irradiation of ^{235}U with Deuterons (2009)

- Expected results

^{235}Np – ~1.7 MBq (~8.4×10^{13} atoms)
^{236m}Np – ~710 MBq (~8.3×10^{13} atoms)
^{236g}Np – ~2 Bq (~1.4×10^{13} atoms)
^{237}Np – ~0.03 Bq (~3×10^{12} atoms)

^{236}Pu – ~300 kBq (3.9×10^{13} atoms from ^{236m}Np decay)
^{238}Pu – <20 Bq (<6.4×10^{10} atoms)
^{239}Pu – <1 Bq (<2.5×10^{11} atoms)
^{240}Pu – <1 Bq (<3×10^{8} atoms)

…and 2.7×10^{16} fissions

Irradiation of ^{235}U with Deuterons (2009)

- Expected outcomes

  Better purity data for ^{236}Pu

  Useable source of ^{235}Np

  Fission products – ^{91}Y, ^{95}Zr, ^{106}Ru, ^{144}Ce, ^{147}Nd

Irradiation of ^{235}U with Deuterons (2010)

- Possible irradiation

^{235}U enrichment: 99.994%

(^{233}U – <0.006%, ^{234}U – <0.006%,
^{236}U – <0.006**%, ^{238}U – <0.006%**)*

Amount irradiated: 1.0 grams
Incident energy: 19 MeV
Target thickness: ~320 mg/cm^2
Irradiation time: 20 hours
Target backing: Copper

* - upper limit

Irradiation of ^{235}U with Deuterons (2010)

- Expected results

^{235}Np – ~1.4 MBq (~7×10^{13} atoms)

^{236m}Np – ~590 MBq (~6.9×10^{13} atoms)

^{236g}Np – ~2 Bq (~1.2×10^{13} atoms)

^{237}Np – ~0.03 Bq (~2.5×10^{12} atoms)

^{236}Pu – ~250 kBq (3.3×10^{13} atoms from ^{236m}Np decay)

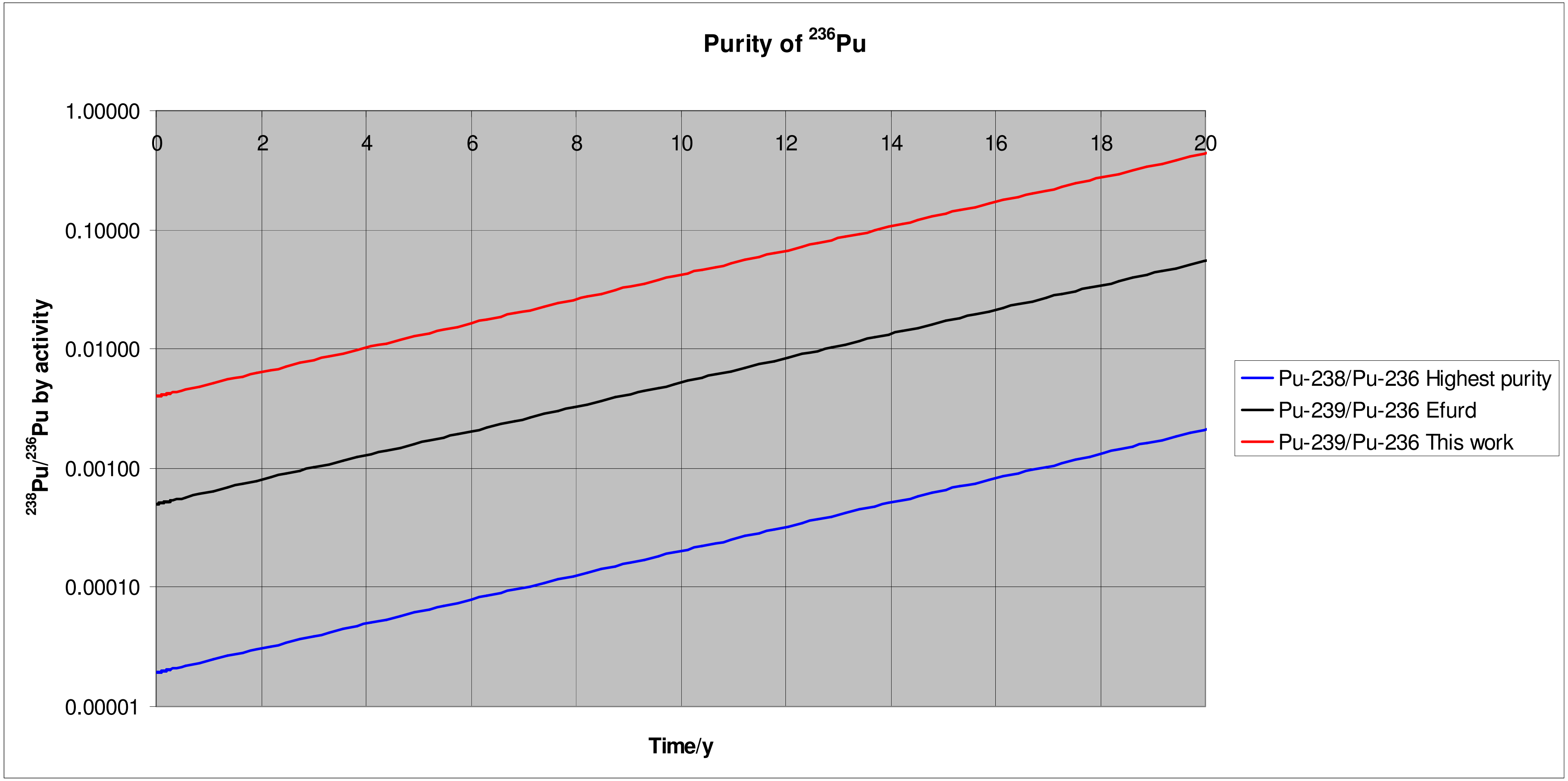
^{238}Pu – <200 Bq (<5.3×10^{11} atoms)

^{239}Pu – <3 Bq (<2.1×10^{12} atoms)

^{240}Pu – <1 Bq (<2.5×10^{9} atoms)

…and 2.3×10^{16} fissions

Irradiation of ^{235}U with Deuterons (2010)



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Irradiation of ^{237}Np with γ (2010)

- Experimental

Irradiate Tungsten or Tantalum target in a LINAC to produce high energy γ photons

Irradiate pure ^{237}Np as NpO_2 in photon flux

Produce ^{236m}Np, allow to decay:

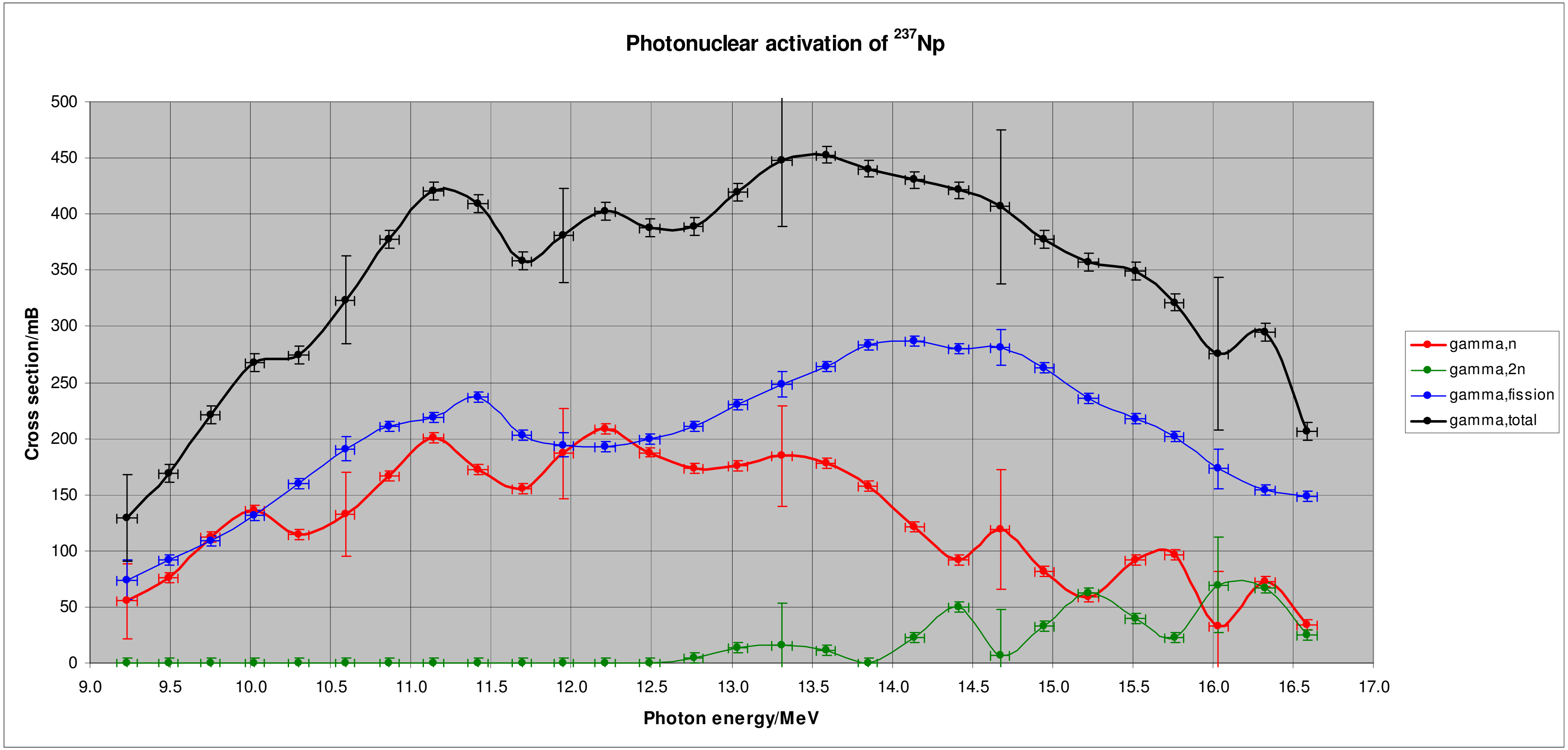
$^{237}Np(\gamma,n)^{236m}Np(\beta)^{236}Pu$

Advantages – fewer fission products

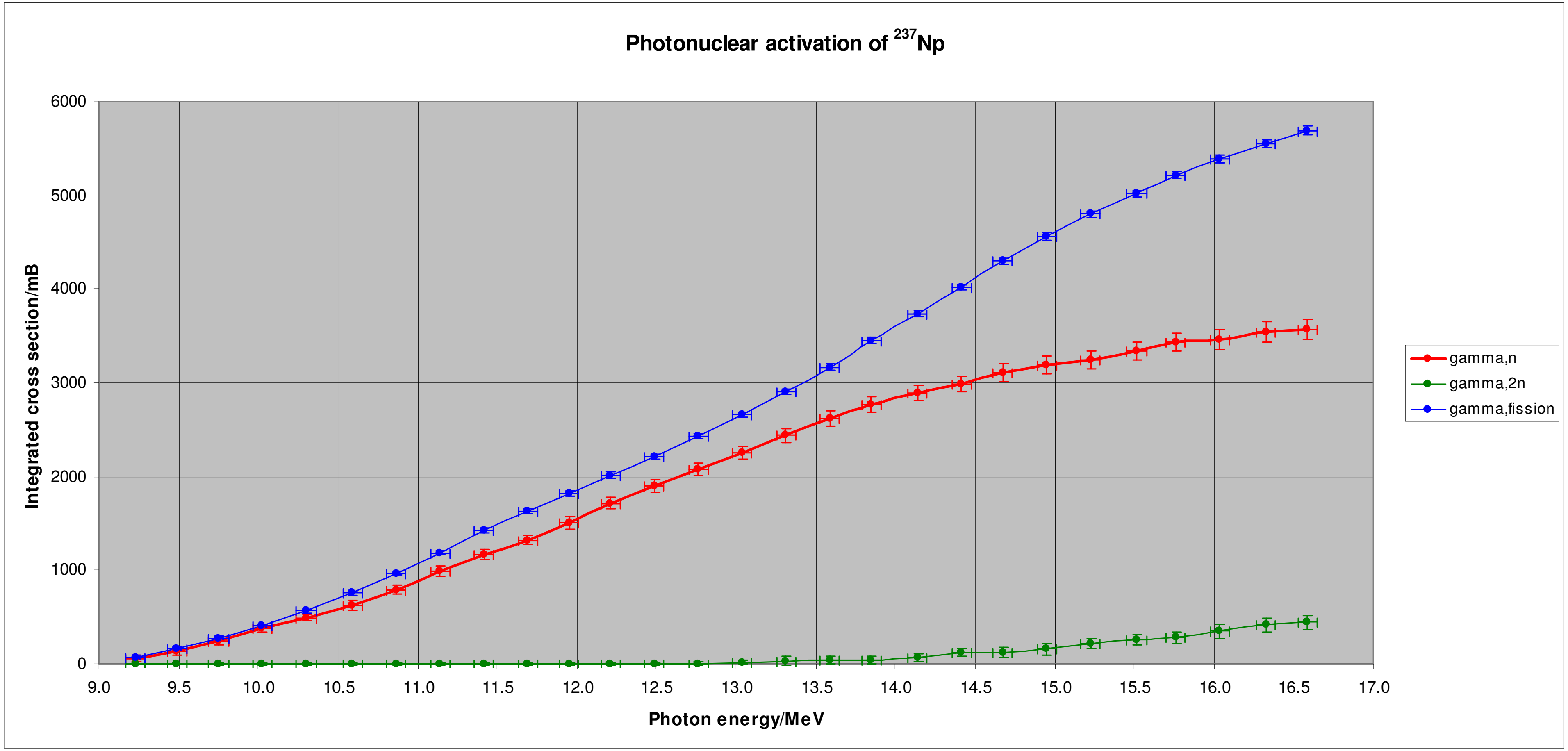
Disadvantages – possible to produce ^{238}Pu via

$^{237}Np(n,\gamma)^{238}Np(\beta)^{238}Pu$

Irradiation of ^{237}Np with γ (2010)



Irradiation of ^{237}Np with γ (2010)



Irradiation of ^{237}Np with γ (2010)

- NPL research LINAC

  Beam current up to 1 mA

  Energy available 18-20 MeV

  We hold ~500 mg pure ^{237}Np as NpO_2 for such work

  Discrepancy between reported production rates:

  ~3900 Bq/g/μA/h reported by Dmitriev *et al*

  ~150 Bq/g/μA/h measured at UKAEA

Irradiation of ^{237}Np with γ (2010)

- Next irradiation

  ^{237}Np enrichment: >99.99%
  Amount irradiated: 0.1 grams
  Incident energy: Up to19 MeV
  Irradiation time: 10 hours
  Target backing: Copper

  Fewer fission products (~300 times)
  Much higher amount of ^{237}Np to exclude

Irradiation of ^{237}Np with γ (2010)

- Expected results

^{235}Np – ~100 kBq (~5.2×10^{12} atoms)
^{236m}Np – ~360 MBq (~4.2×10^{13} atoms)
^{236g}Np – ~1 Bq (~7×10^{12} atoms)
^{237}Np – ~13 MBq (~1.3×10^{21} atoms)

^{236}Pu – ~150 kBq (2×10^{13} atoms from ^{236m}Np decay)
^{238}Pu – <20 Bq (<5.3×10^{10} atoms)
^{239}Pu – <1 Bq (<7×10^{11} atoms)
^{240}Pu – <1 Bq (<2.5×10^{9} atoms)

…and 6.7×10^{13} fissions

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Thank You

Any questions?