

Safe Handling of Radioisotopes

— Chemistry —

Fundamental Radiochemistry

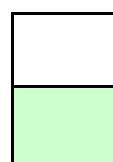
Nuclides, Radioactive decay, Decay series, Natural radionuclides,
Nuclear reactions, Radiation effect

Department of Chemistry

Yasuji Oura

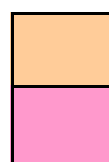
1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Stable elements

Natural radioactive elements



Having natural radioactive isotopes

Artificial radioactive elements

Naming Elements 114 and 116 (2016):

Nh (Nihonium) Mc (Moscovium) Ts (Tennessine) Og (Oganesson)

Discovery of element 113 at RIKEN (2004, 2012)

^{209}Bi is a radionuclide. $[(1.9 \pm 0.2) \times 10^{19} \text{ years}]$ (2003)

mass number = $Z + N$

atomic number =
number of protons

Symbol of
element



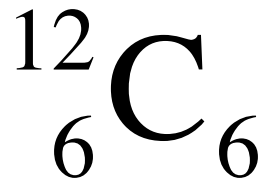
Nuclide

number of neutrons

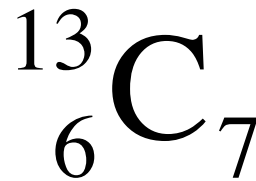
Z: isotope

N: isotone

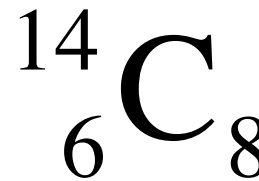
A: isobar



stable

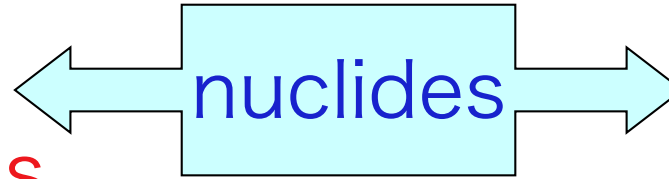


stable



radioactive

unstable nuclides
= radionuclides

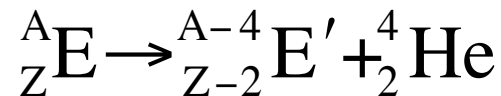


stable nuclides

Radionuclide changes to the other nuclide spontaneously by radioactive decay.

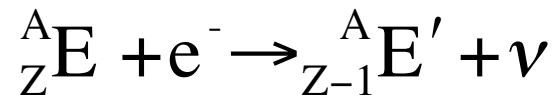
Release energy to transfer to more stable state.

α decay



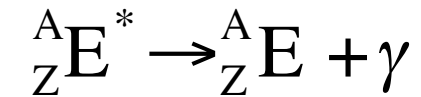
α -ray

β decay



β -ray, γ -ray

γ decay



Isomeric Transition

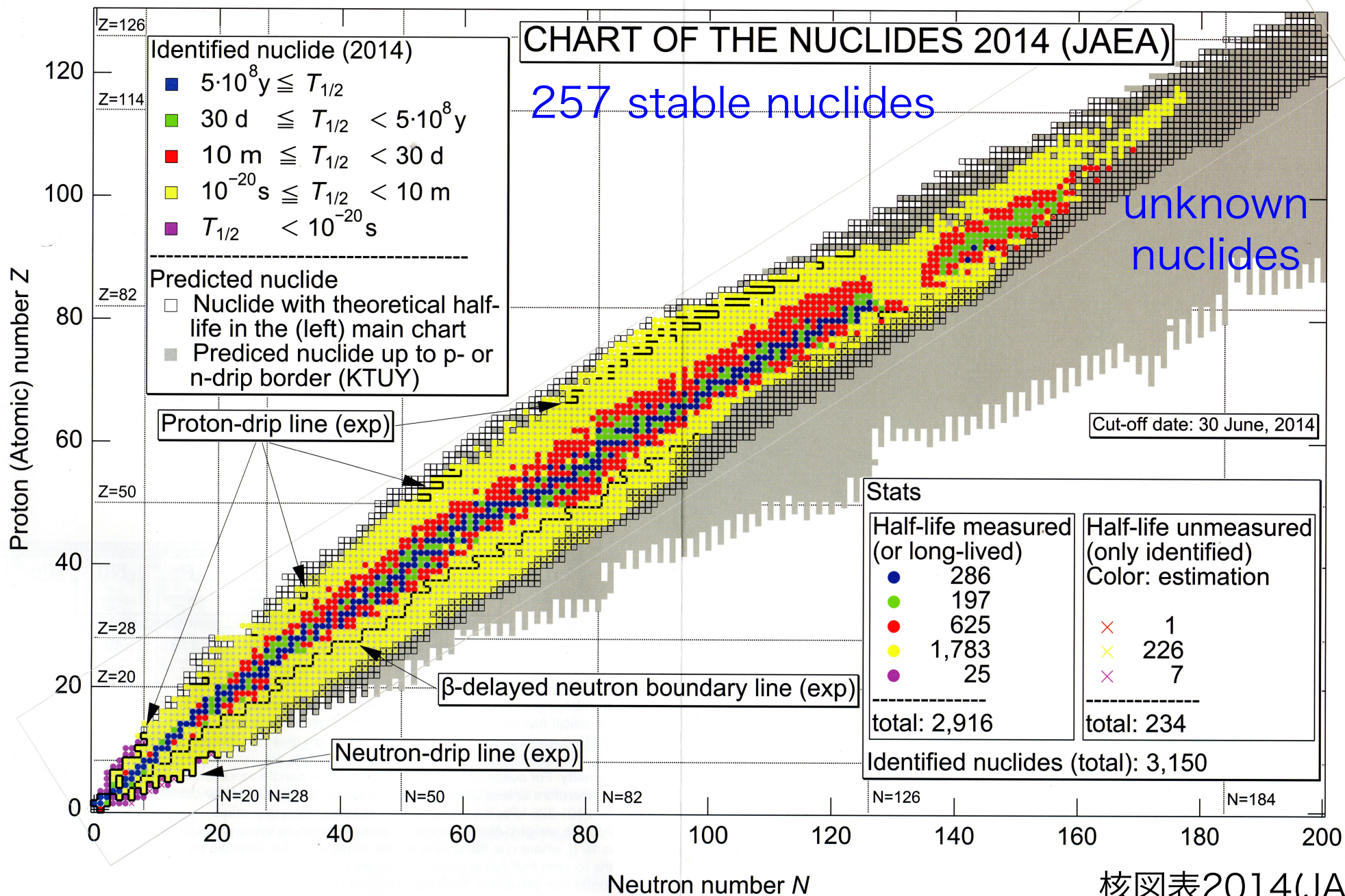
γ -ray

conversion electron

自発核分裂

neutron

Nuclide Chart



Radioactive decay

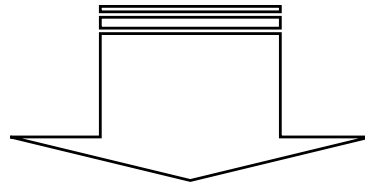
probabilistic events

decay speed :

*number of decaying
nuclides per unit time*

$$-\frac{dN}{dt} = \lambda N$$

N : number of radionuclides, λ : decay constant, t : time



$$N = N_0 e^{-\lambda t}$$

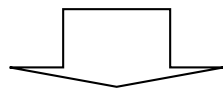
N_0 : N at $t = 0$

Half Life

$$N = N_0 e^{-\lambda t}$$

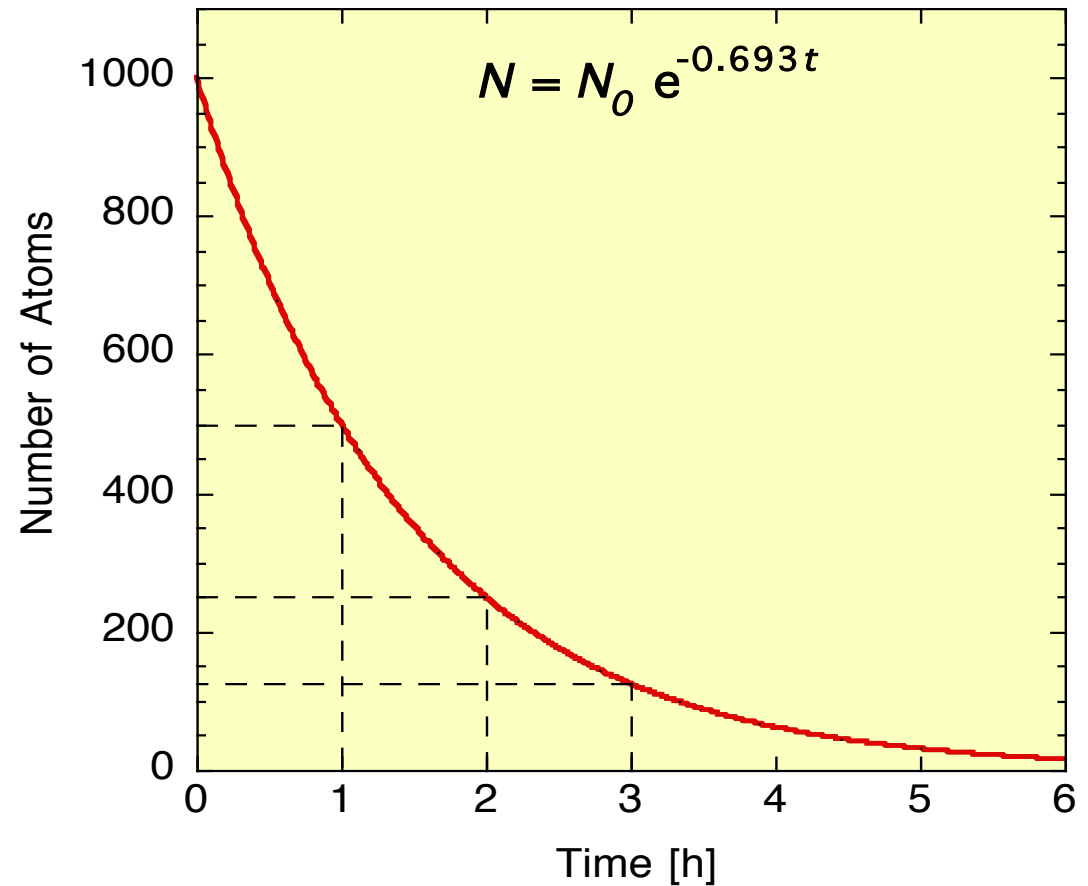
The time required for number of nuclides, N_0 , to decrease to $N_0/2$:
 $T_{1/2}$

$$\frac{1}{2} N_0 = N_0 e^{-\lambda T_{1/2}}$$



$$T_{1/2} = \frac{\ln 2}{\lambda}$$

$$N = N_0 \left(\frac{1}{2} \right)^{t/T_{1/2}}$$



Radioactivity

number of nuclides decaying per unit time

Unit: becquerel (Bq),

number of nuclides decaying a second

curie (Ci): radioactivity of 1 g of ^{226}Ra
 $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$

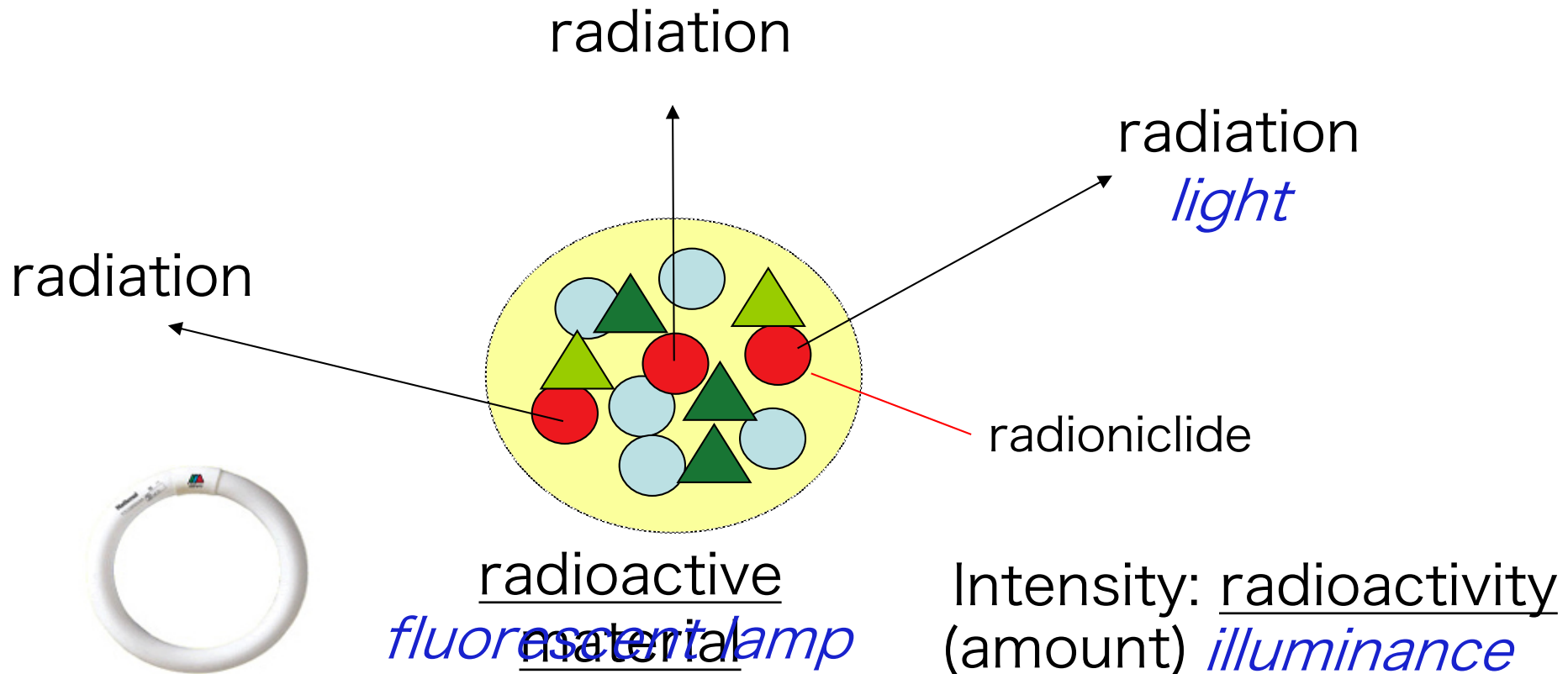
$$A = \lambda N = -dN / dt$$

A: radioactivity [Bq], λ : decay constant [s^{-1}],

N: number of nuclides

$$A = A_0 e^{-\lambda t}$$

- radioactive materials (radionuclides, materials including radionuclide(s))
- radiation
- radioactivity (amount of radionuclides, not term showing materials)



(Ex.) Radioactivity of potassium $A = \lambda N$

^{39}K : 93.3 %, ^{40}K : 0.012 %, ^{41}K : 6.7 %

$T_{1/2}$: 1.28×10^9 years

^{40}K in 1 g of K,

$$\left(\frac{0.693}{1.28 \times 10^9 \times 365 \times 24 \times 3600} \right) \times \left(\frac{1}{39.1} \times 6.02 \times 10^{23} \times 0.012 \times 10^{-2} \right)$$

= 32 Bq

K concentration in a body = 0.35 %

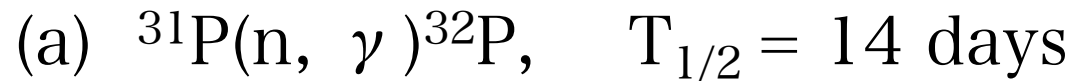
if weight = 60 , 6.7 kBq

<p>32 Bq/gK Specific radioactivity</p>
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Specific radioactivity [Bq / g]

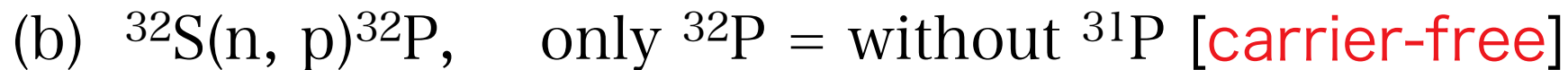
radioactivity per unit mass of element with its radioisotope

^{32}P :



If 1 mg of P is irradiated, 60 MBq of ^{31}P is produced.

$$\rightarrow 6 \times 10^4 \text{ MBq/g}$$



$$60 \text{ MBq} = 1.0 \times 10^{14} \text{ atoms} = 5.2 \times 10^{-9} \text{ g}$$

$$\rightarrow 1.2 \times 10^{10} \text{ MBq/g}$$

$$A_s = \frac{A}{W} = \frac{A}{(A/\lambda)/N_A \times M} = \frac{\lambda \times N_A}{M} \quad \text{constant not depending on time}$$

Specific radioactivity [Bq / g]

radioactivity per unit mass of element with its radioisotope



Radioactivity concentration

[Bq / g, Bq / mL]

radioactivity per unit mass of material (sample) including radionuclide

^{40}K in a human body

^{137}Cs in a food

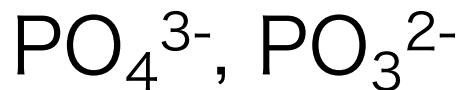
Purity

chemical purity = $\frac{\text{amount of interested chemical species with radionuclide}}{\text{total amount of a sample}}$

radionuclidic purity = $\frac{\text{radioactivity of a interested radionuclide}}{\text{total radioactivity in a sample}}$
(radiopurity)



radiochemical purity = $\frac{\text{radioactivity of radionuclide in a specific chemical form}}{\text{total radioactivity of the radionuclide}}$



Purity

chemical purity = $\frac{\text{amount of interested chemical species with radionuclide}}{\text{total amount of a sample}}$

↑
Content of Target Element
Irrelevant radioactivity

Ex. If the weight of Cu in a 1.00 g sample containing a small amount of Ni and Zn is 0.99 g, the **chemical purity** is 99%.

radionuclidic purity = $\frac{\text{radionuclide}}{\text{total radioactivity in a sample}}$
(radiopurity)

^{32}P , ^{33}P

radiochemical purity = $\frac{\text{radioactivity of radionuclide in a specific chemical form}}{\text{total radioactivity of the radionuclide}}$

PO_4^{3-} , PO_3^{2-}

Purity

chemical purity = $\frac{\text{amount of interested chemical species with radionuclide}}{\text{total amount of a sample}}$

radionuclidic purity (radiopurity) = $\frac{\text{radioactivity of a interested radionuclide}}{\text{total radioactivity in a sample}}$

^{32}P , ^{33}P

radiochemical purity =

PO_4^{3-} , PO_3^{2-}

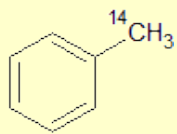
Ex. ^{60}Co : 100 Bq	} Radionuclidic Purity of ^{60}Co 50%
^{137}Cs : 10 Bq	
^{131}I : 90 Bq	
<hr/> Total 200 Bq	

radionuclide

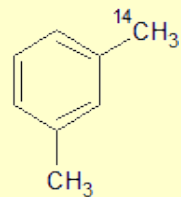
Purity

chemical purity = $\frac{\text{amount of interested chemical species with radionuclide}}{\text{total amount of a sample}}$

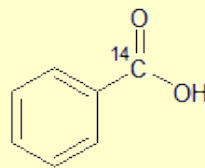
Ex.



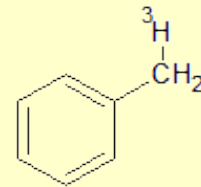
Toluene [¹⁴C]
40 Bq



Xylene [¹⁴C]
10 Bq



Benzoic Acid [¹⁴C]
100 Bq

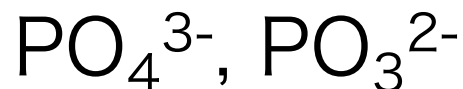


Toluene [³H]
50 Bq

Radiochemical Purity
of Benzoic Acid [¹⁴C]

$$\frac{100}{(40 + 10 + 100)} \times 100 = 66.67\%$$

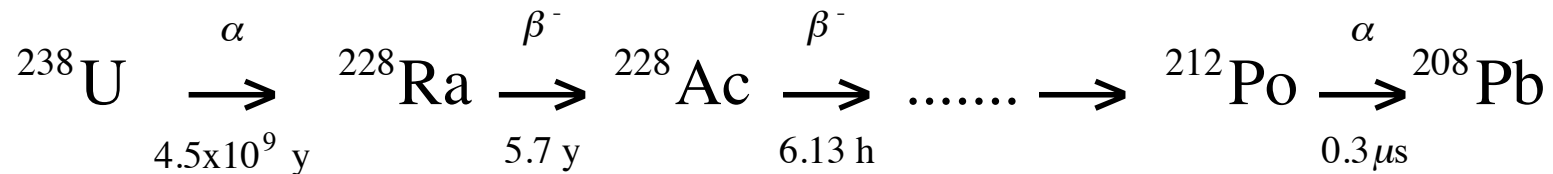
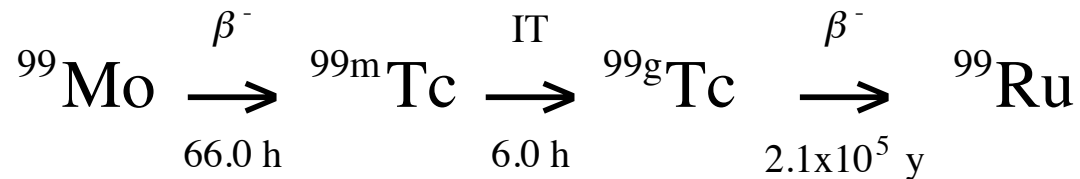
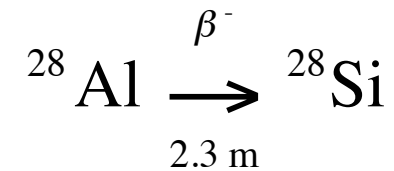
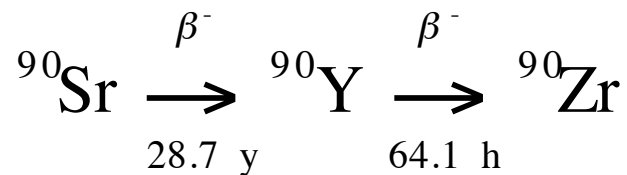
radiochemical
purity =



$\frac{\text{radioactivity of radionuclide in a specific chemical form}}{\text{total radioactivity of the radionuclide}}$

Decay series

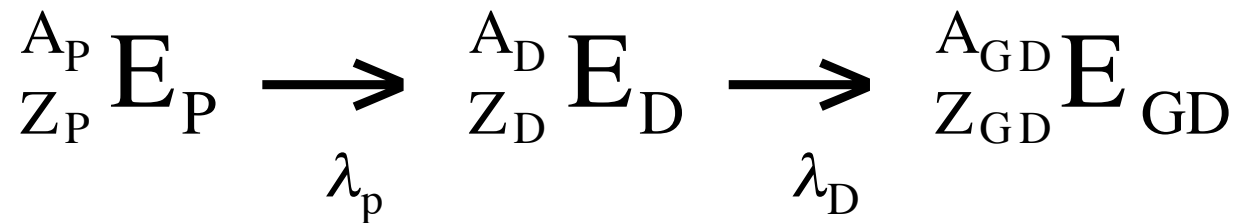
When decay products are radionuclides, decay occurs continuously. The sequence of nuclides that cause this series of decay is called decay series.



parent daughter granddaughter

Radioactive Equilibrium

Decay rate of radionuclides in a decay series



$$t = 0; \quad N_P^0 \quad N_D^0 \quad N_{GD}^0$$

$$t; \quad N_P \quad N_D \quad N_{GD}$$

$$\frac{dN_P}{dt} = -\lambda_P N_P$$

$$\frac{dN_D}{dt} = -\lambda_D N_D + \lambda_P N_P$$

Radioactive Equilibrium

$$\frac{dN_P}{dt} = -\lambda_P N_P$$

$$\frac{dN_D}{dt} = \lambda_P N_P - \lambda_D N_D$$

$$\left\{ \begin{array}{l} N_P = N_P^0 e^{-\lambda_P t} \\ N_D = \frac{\lambda_P}{\lambda_D - \lambda_P} N_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) + N_D^0 e^{-\lambda_D t} \end{array} \right.$$

multiply λ_P or λ_D on both sides

$$\left\{ \begin{array}{l} A_P = A_P^0 e^{-\lambda_P t} \\ A_D = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) + A_D^0 e^{-\lambda_D t} \end{array} \right.$$

Radioactive Equilibrium

$$\left\{ \begin{array}{l} A_P = A_P^0 e^{-\lambda_P t} \\ A_D = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) + A_D^0 e^{-\lambda_D t} \end{array} \right.$$

$$1) \lambda_P < \lambda_D \quad [T_{1/2}^P > T_{1/2}^D]$$

$$2) \lambda_P \ll \lambda_D \quad [T_{1/2}^P \gg T_{1/2}^D]$$

$$3) \lambda_P > \lambda_D \quad [T_{1/2}^P < T_{1/2}^D]$$

where $A_D^0 = 0$

$$1) \lambda_P < \lambda_D \quad [T_{1/2}^P > T_{1/2}^D] \quad \left\{ \begin{array}{l} A_P = A_P^0 e^{-\lambda_P t} \\ A_D = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) \end{array} \right.$$

After enough time, $e^{-\lambda_P t} \gg e^{-\lambda_D t}$

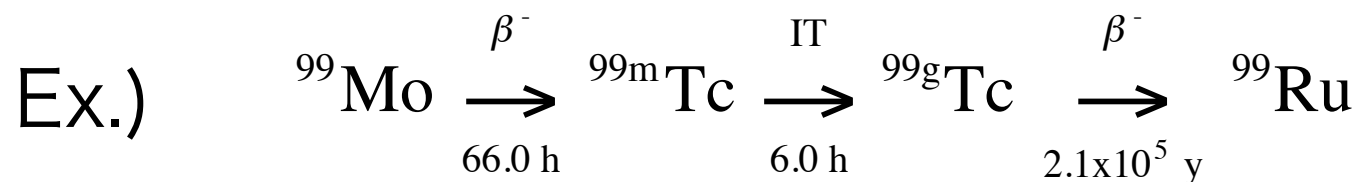
$$A_D \approx \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 e^{-\lambda_P t} = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P$$

$$\frac{A_D}{A_P} = \frac{\lambda_D}{\lambda_D - \lambda_P}$$

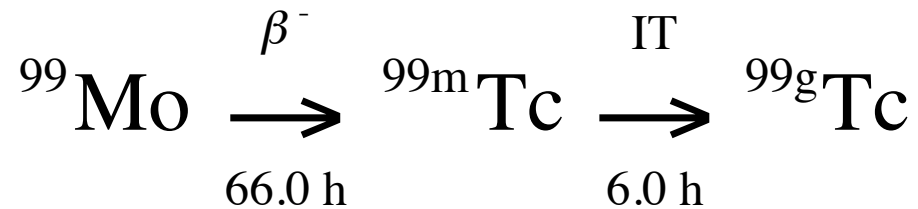
Radioactivity ratio of daughter to parent nuclides is equal.

||

transient equilibrium



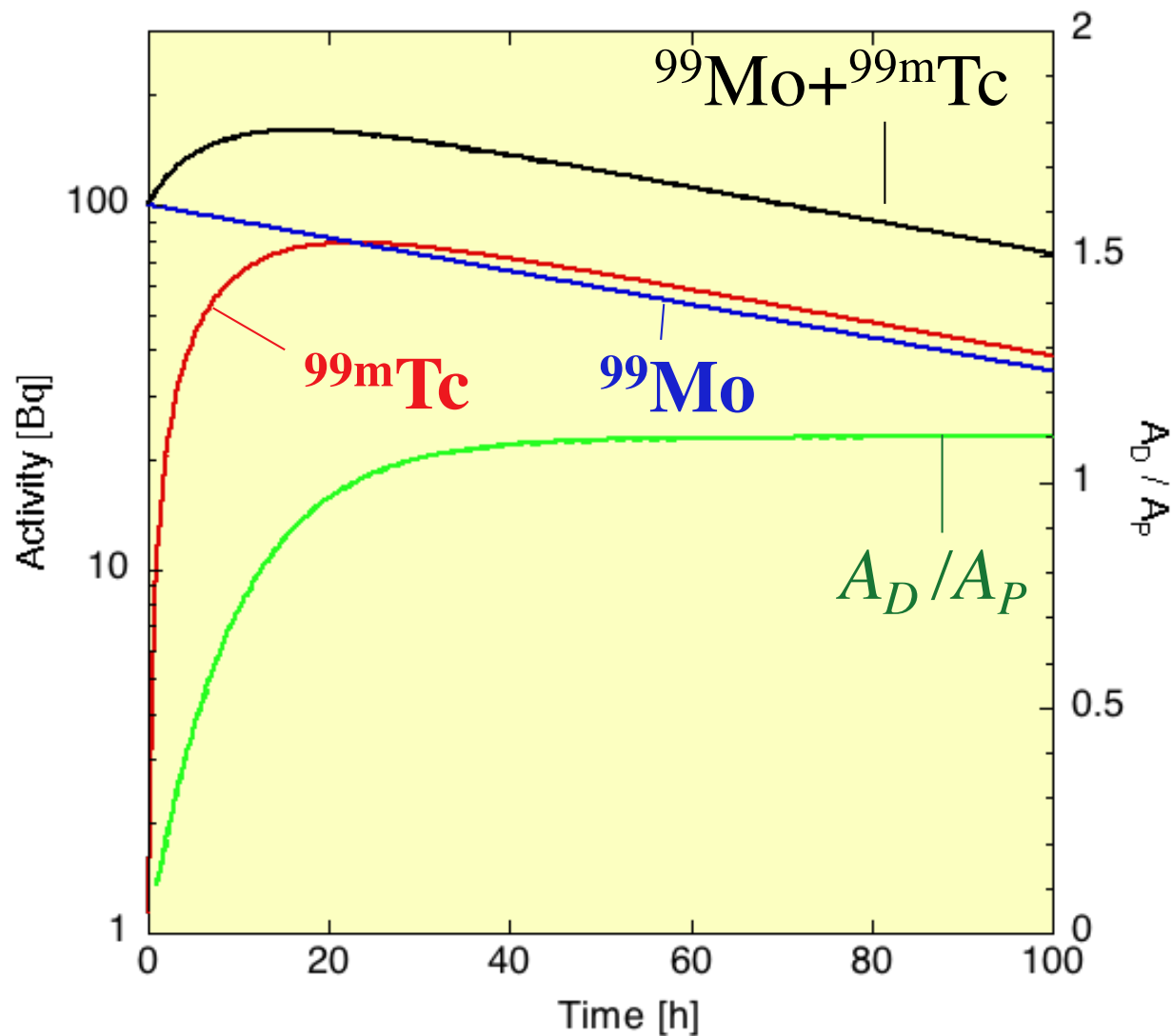
Transient Equilibrium



$$\frac{A_D}{A_P} = \frac{\lambda_D}{\lambda_D - \lambda_P}$$

In the case of ${}^{99}\text{Mo} \rightarrow {}^{99\text{m}}\text{Tc}$,

$$A_D/A_P = 1.1$$



$$2) \lambda_P \ll \lambda_D \quad [T_{1/2}^P \gg T_{1/2}^D] \quad \left\{ \begin{array}{l} A_P = A_P^0 e^{-\lambda_P t} \\ A_D = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) \end{array} \right.$$

After enough time, $e^{-\lambda_P t} \gg e^{-\lambda_D t}$. And, $\lambda_D - \lambda_P \approx \lambda_D$

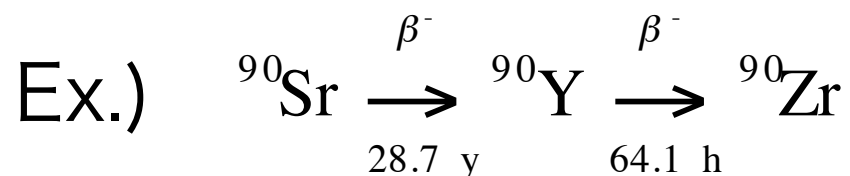
$$A_D \approx \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 e^{-\lambda_P t} = \frac{\lambda_D}{\lambda_D - \lambda_P} A_P \approx \frac{\lambda_D}{\lambda_D} A_P$$

$$A_D = A_P$$

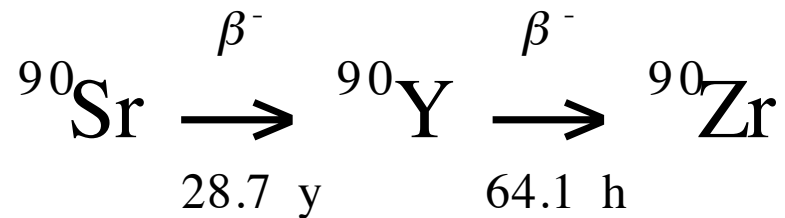
Radioactivity of parent and daughter nuclides are equal.

||

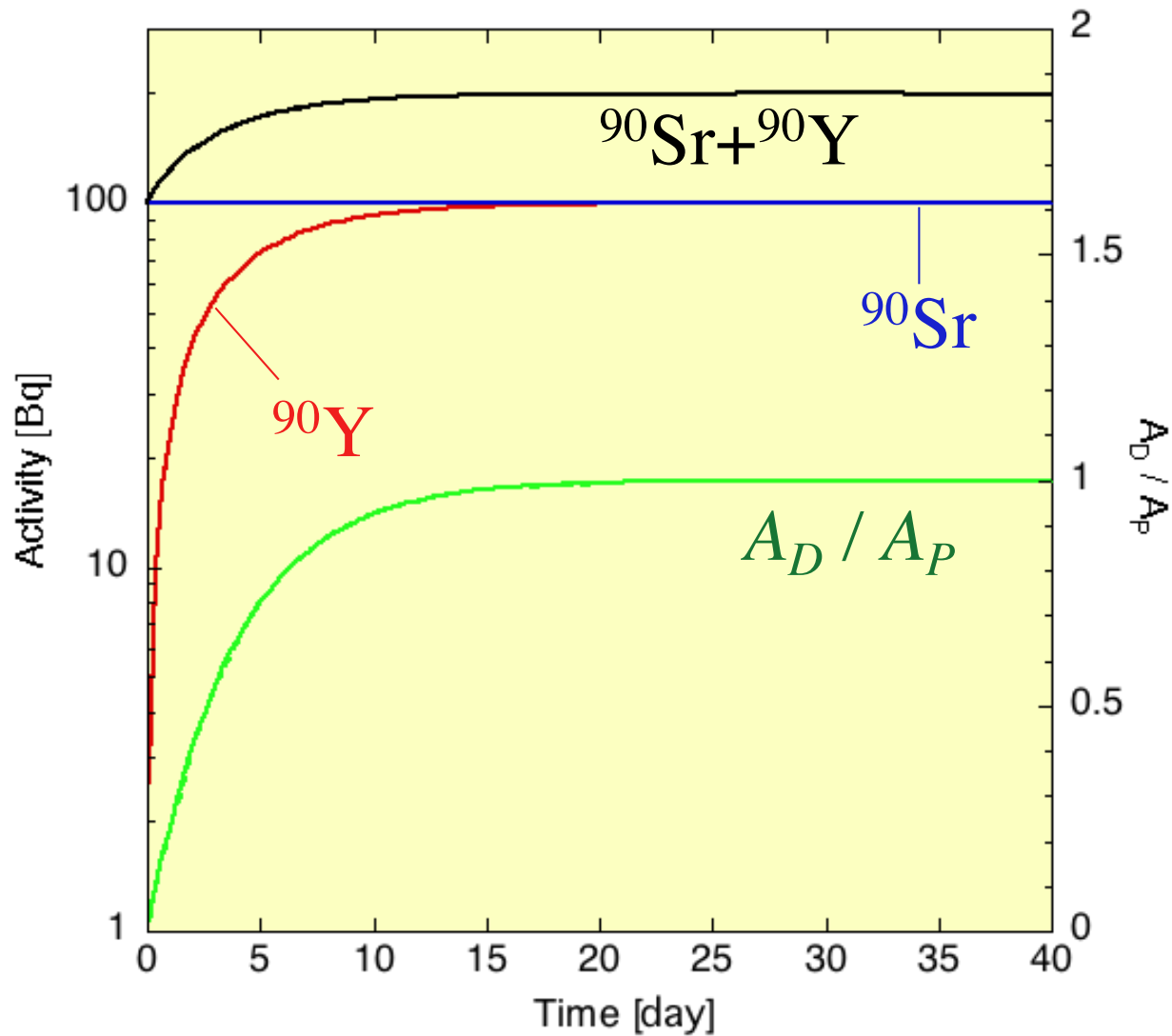
secular equilibrium



Secular Equilibrium



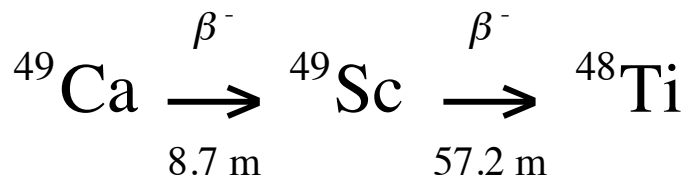
$$A_D = A_P$$



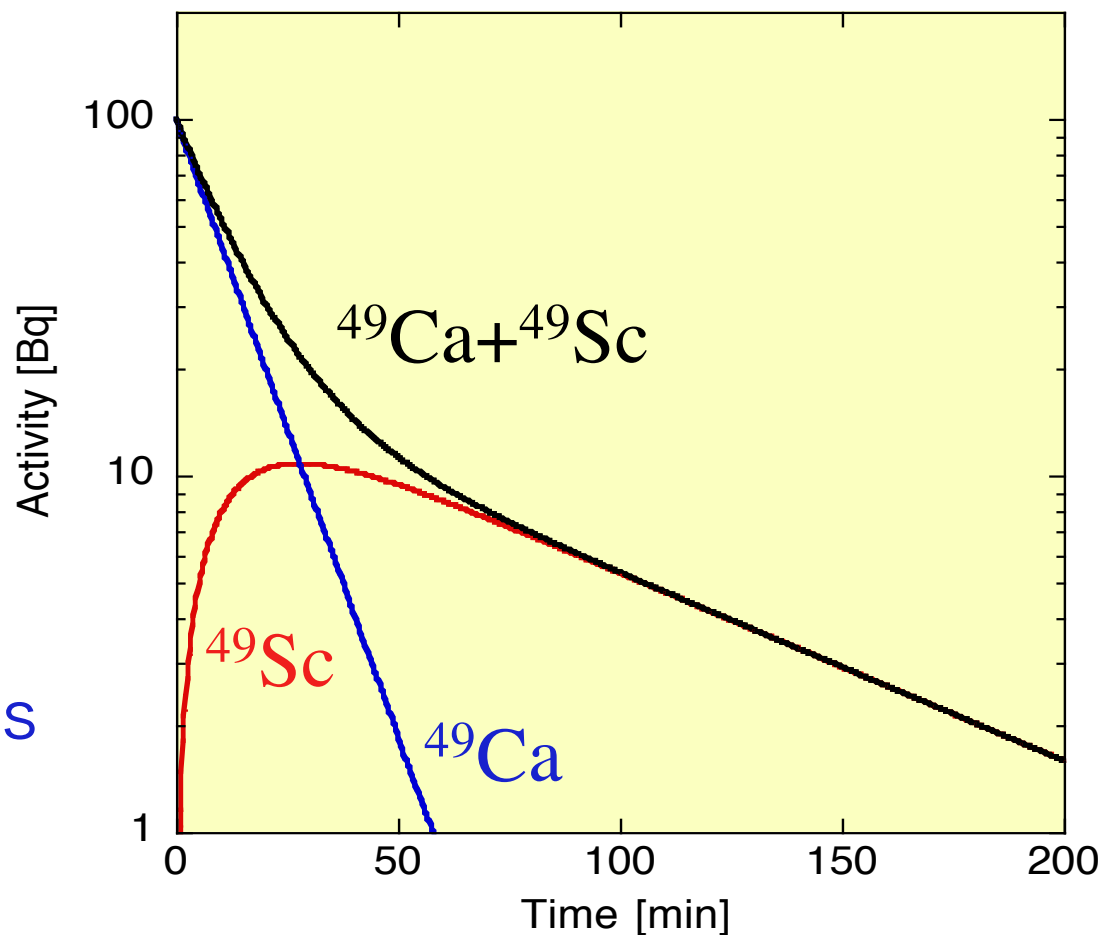
3) $\lambda_P > \lambda_D$

$$[T_{1/2}^P < T_{1/2}^D]$$

$$\left\{ \begin{aligned} A_P &= A_P^0 e^{-\lambda_P t} \\ A_D &= \frac{\lambda_D}{\lambda_D - \lambda_P} A_P^0 (e^{-\lambda_P t} - e^{-\lambda_D t}) \end{aligned} \right.$$

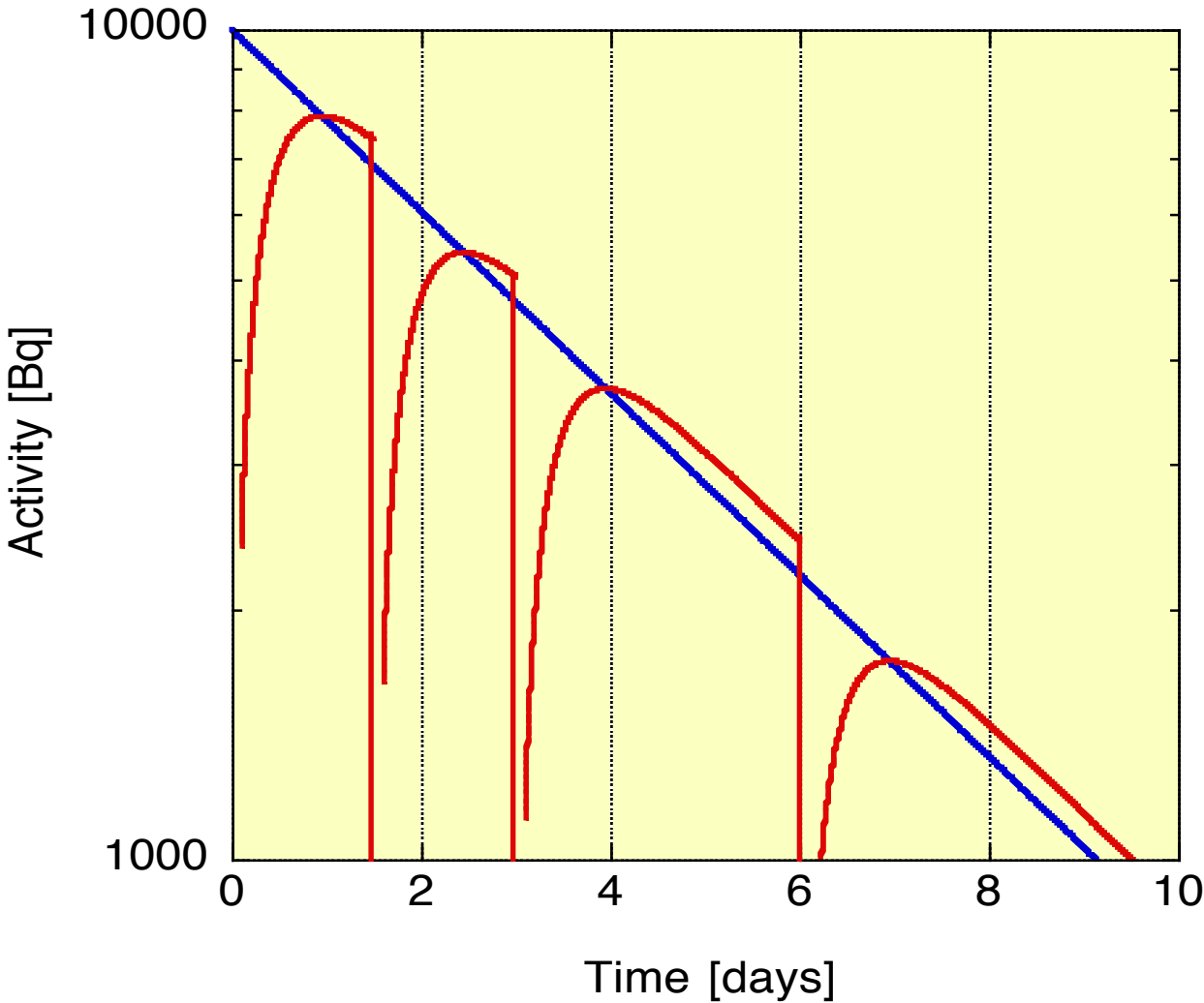
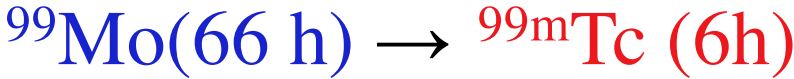


Radioactive equilibrium is not established.



Milking

Using radioactive equilibrium, daughter nuclide that is produced from parent nuclide is extracted repeatedly.



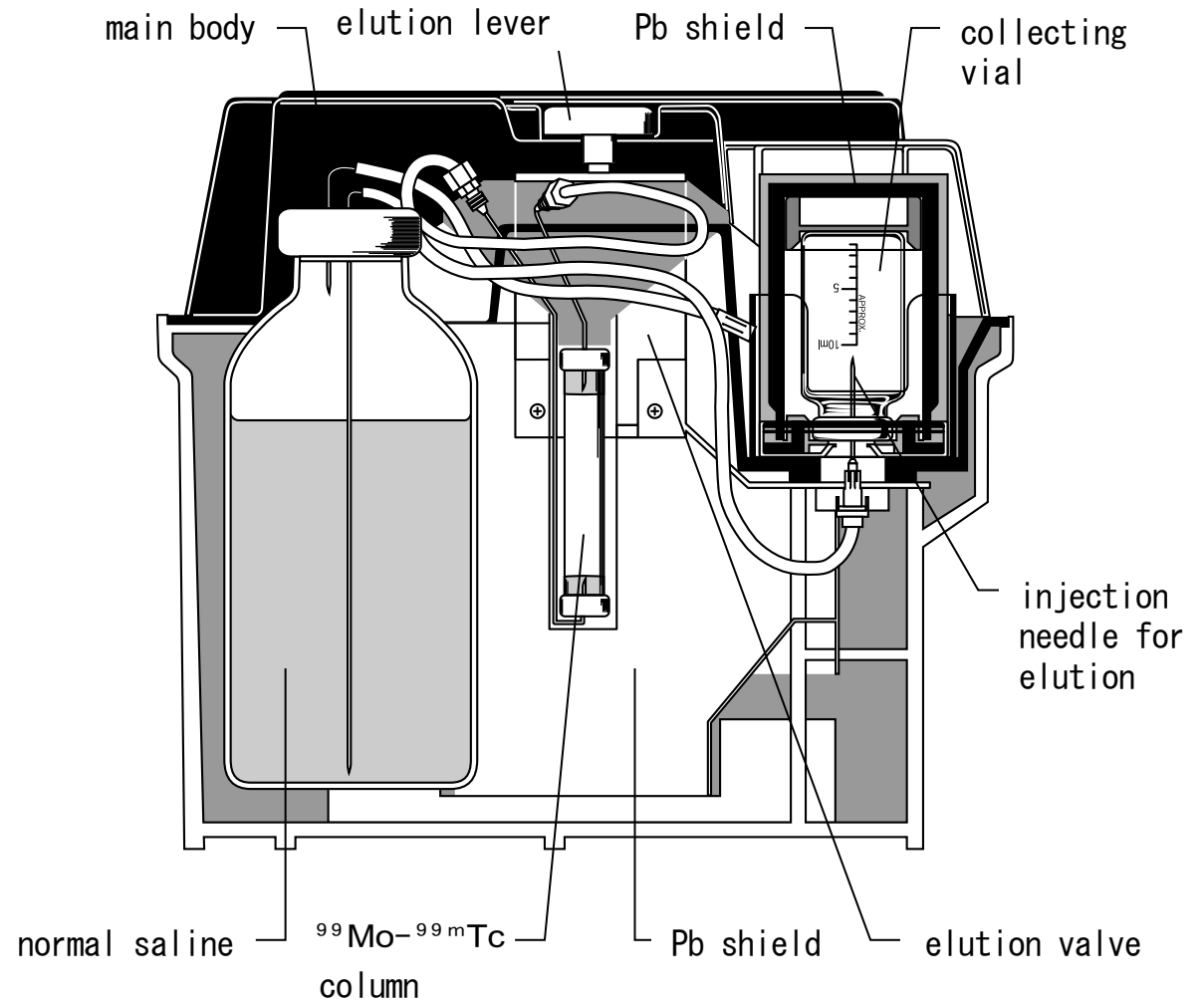
Tc generator
important in
nuclear medicine



<http://fri.fujifilm.co.jp/med/products/diagnosis/brain/utk/>

Tc generator

< Elution Route >







http://fri.fujifilm.co.jp/med/products/diagnosis/brain/utk/pack/pdf/fri_med_utk_attach.pdf

Natural radionuclides

- Primordial radionuclides
- Secondary radionuclides
- Induced radionuclides

1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

	Stable elements		Having natural radioactive isotopes
	Natural radioactive elements		Artificial radioactive elements

Primordial radionuclides

Nuclides that already existed when the solar system was formed and that still exist due to its long half life.

- *Parents of decay series*

^{238}U (4.5×10^9 y), ^{235}U (7.0×10^8 y), ^{232}Th (1.4×10^{10} y)

- *Independent*

^{40}K (1.3×10^9 y)

^{50}V (1.4×10^{17} y)

^{87}Rb (4.8×10^{10} y)

^{115}In (4.4×10^{14} y)

^{123}Te (1.2×10^{13} y)

^{138}La (1.1×10^{11} y)

^{142}Ce ($>5 \times 10^{15}$ y)

^{144}Nd (2.3×10^{15} y)

^{147}Sm (1.1×10^{11} y)

^{148}Sm (7×10^{15} y)

^{152}Gd (1.1×10^{14} y)

^{176}Lu (3.8×10^{10} y)

^{174}Hf (2.0×10^{15} y)

^{187}Re (5×10^{10} y),

^{186}Os (2.0×10^{15} y)

^{190}Pt (6.5×10^{11} y)

Isotopic abundance > 10%

Secondary radionuclides

- Short-lived nuclides belonging to decay series originated in primordial radionuclides.
- Fission products of spontaneous fission

U series: $^{238}\text{U} \rightarrow ^{206}\text{Pb}$, mass number = $4n + 2$

Th series: $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$, mass number = $4n$

Ac series: $^{235}\text{U} \rightarrow ^{207}\text{Pb}$, mass number = $4n + 3$

Induced radionuclides

Nuclides that are always produced in the upper atmosphere mainly by nuclear reactions with cosmic rays in nature.

Nuclear spallation reactions of N and O

^3H (12.3 y), ^7Be (53.3 d), ^{10}Be (1.5×10^6 y),
 ^{14}C (5.7×10^3 y)

Nuclear spallation reactions of Ar

^{22}Na (2.6 y), ^{32}Si (172 y), ^{32}P (14.3 d),
 ^{35}S (87.5 d), ^{36}Cl (3.0×10^5 y)

Induced radionuclides

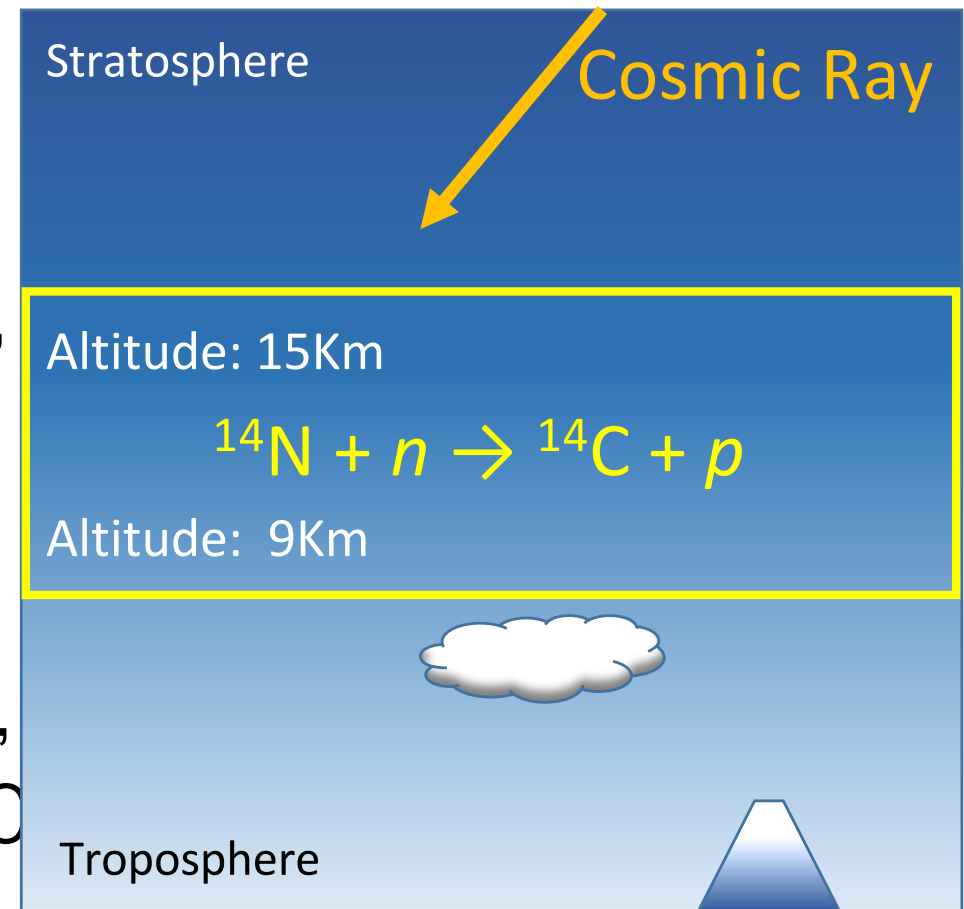
Nuclides that are always produced in the upper atmosphere mainly by nuclear reactions with cosmic rays in nature.

Nuclear spallation reactions

^3H (12.3 y), ^7Be (53.3 d),
 ^{14}C (5.7×10^3 y)

Nuclear spallation reactions

^{22}Na (2.6 y), ^{32}Si (172 y),
 ^{35}S (87.5 d), ^{36}Cl (3.0×10^5 y)

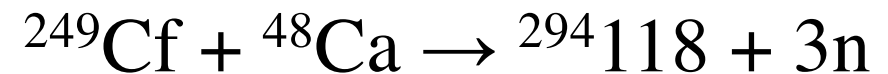
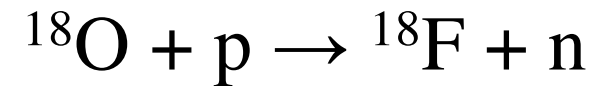
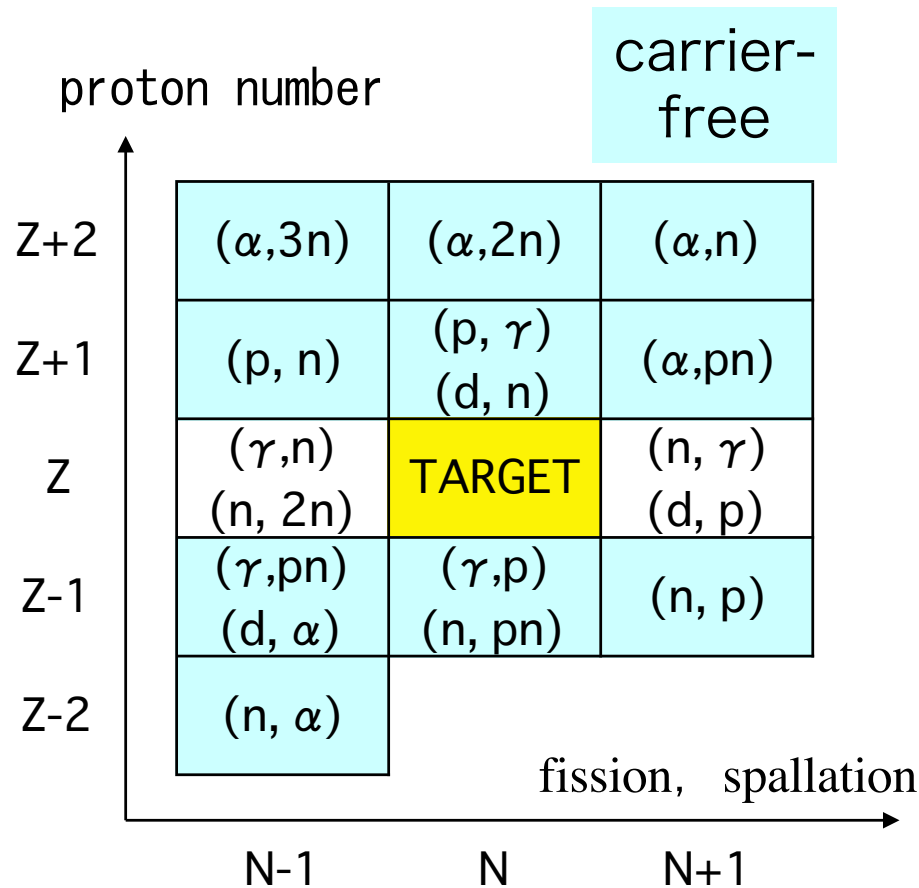


Artificial radionuclides

produced by nuclear reactions

- nuclear reactor (neutrons)
- accelerator (positive ions, electrons)

RI,
radioactive
medicines



Irradiation energy is important.
yields
secondary products

Radioactivity induced by nuclear reaction

$$N = n\phi\sigma t \quad N/n = \phi\sigma t$$

$$A = n\phi\sigma \underbrace{(1 - e^{-\lambda t})}_{\text{saturation factor}}$$

N : number of reactions
 A : induced radioactivity
 n : number of target nuclides
 ϕ : fluence rate
 σ : reaction cross section
 λ : decay constant
 t : irradiation time

(Ex.) $^{31}\text{P}(n,\gamma)^{32}\text{P}$, $T_{1/2} = 14$ days

$$\phi : 10^{13} \text{ cm}^{-2}\text{s}^{-1}$$

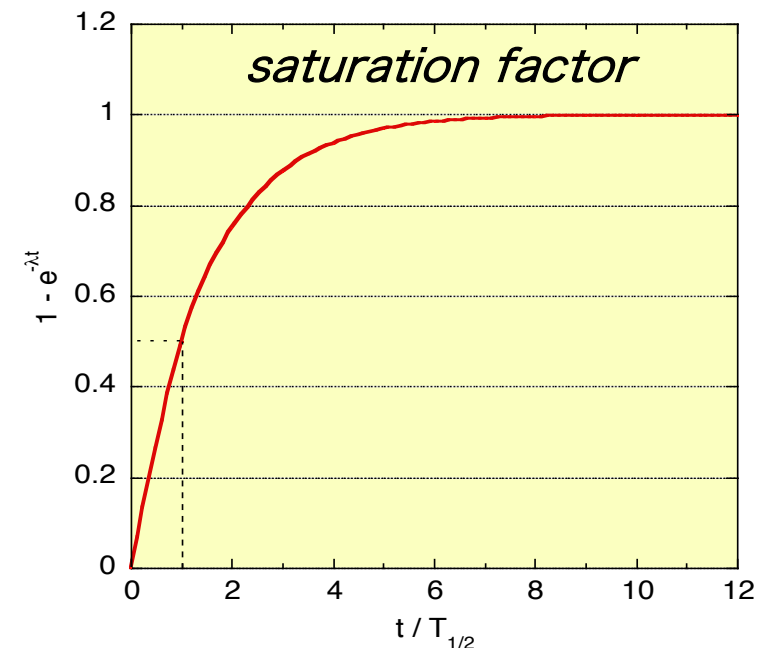
$$\sigma : 0.17 \text{ b} = 0.17 \times 10^{-24} \text{ cm}^2$$

$$\lambda : 0.049 \text{ d}^{-1} = 5.7 \times 10^{-7} \text{ s}^{-1}$$

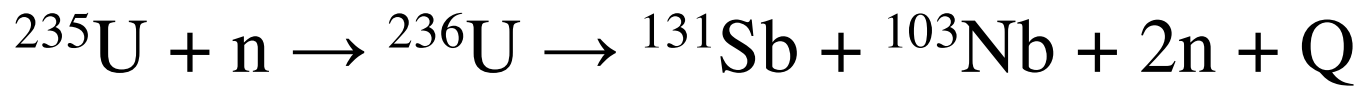
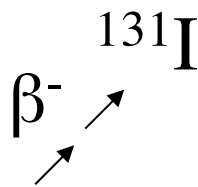
$$t : 14 \text{ d} = 1.2 \times 10^6 \text{ s}$$

$$A = 1.6 \times 10^{10} \text{ Bq/g}$$

$$N/n = 2.0 \times 10^{-6}$$



Nuclear fission



m_i

m_f

$m_i > m_f$

$$Q = (m_i - m_f) \times c^2$$

$$\sim 200 \text{ MeV}$$

$$1 \text{ MeV} = 3.8 \times 10^{-17} \text{ kcal}$$

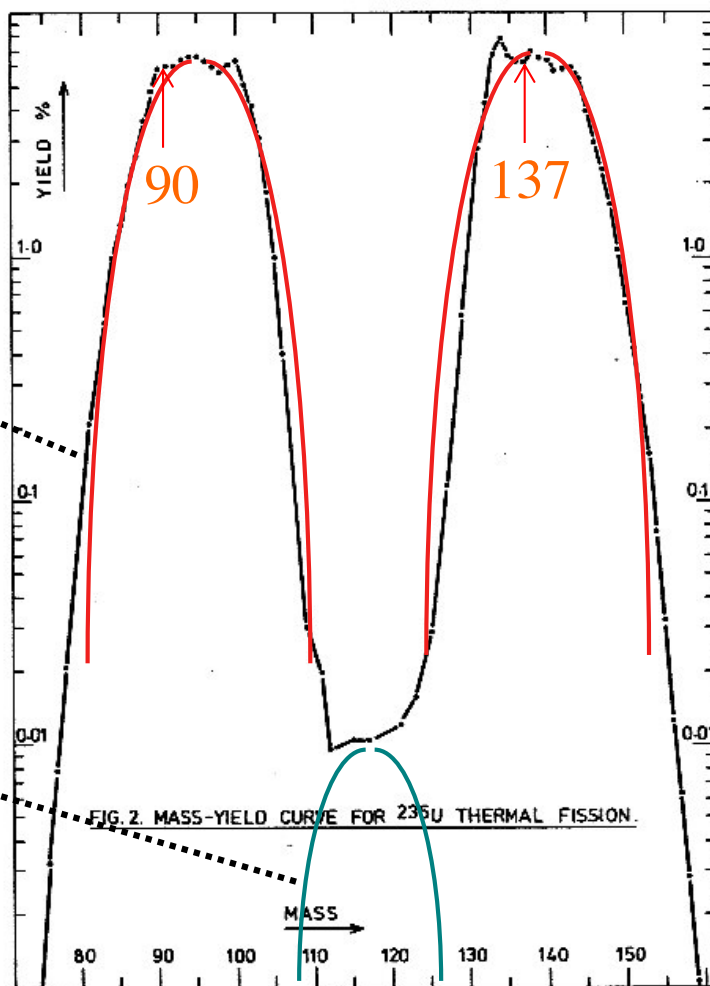
$$1 \text{ g of } ^{235}\text{U} = 2.5 \times 10^{21} \text{ atoms}$$

$$1.9 \times 10^7 \text{ kcal}$$

$$1 \text{ g of coal} = 8.1 \text{ kcal}$$

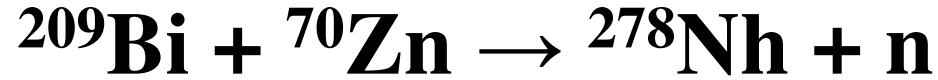
asymmetric fission

symmetric fission

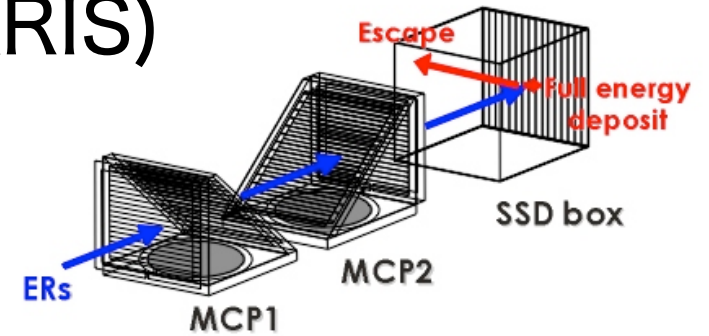
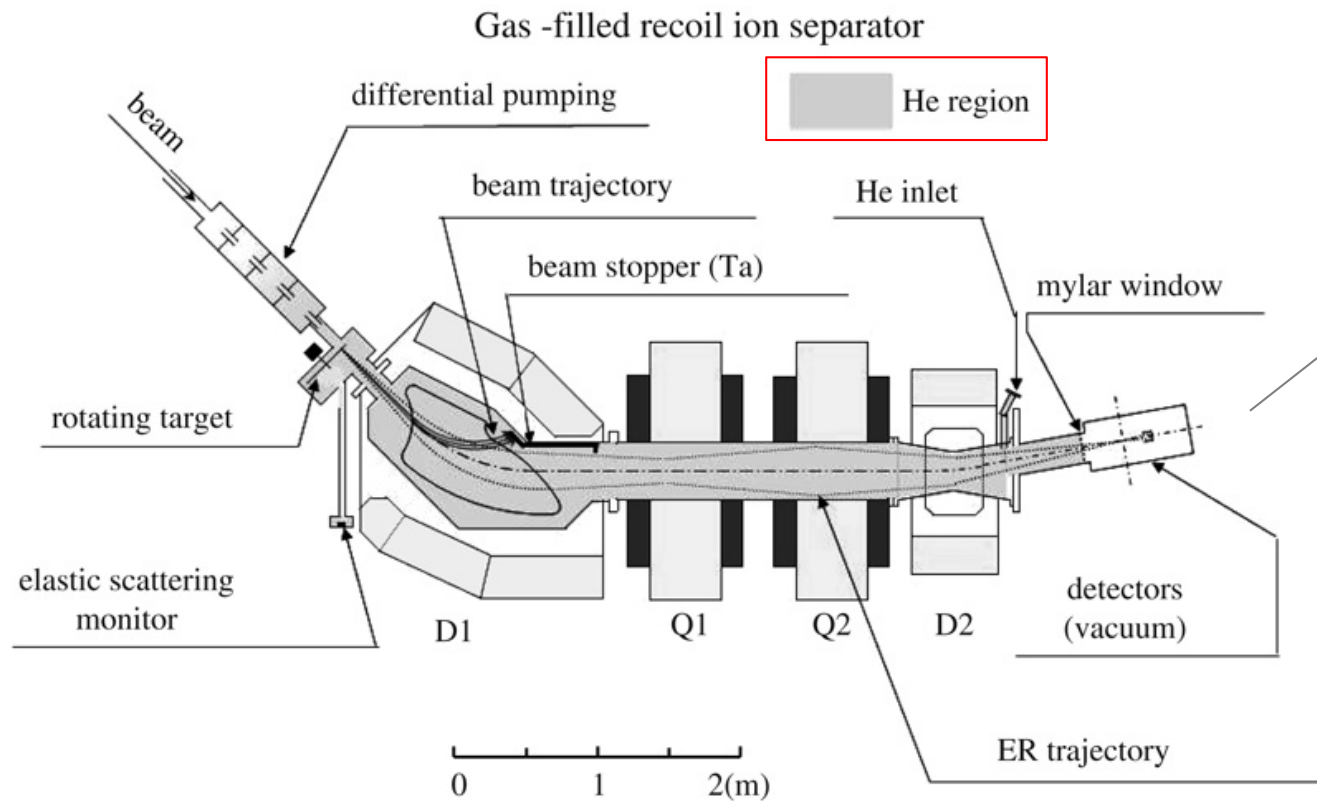


Crouch (1977)

Element 113



Gas-filled Recoil Ion Separator (GARIS)



Charge of ions become same by passing through gas.

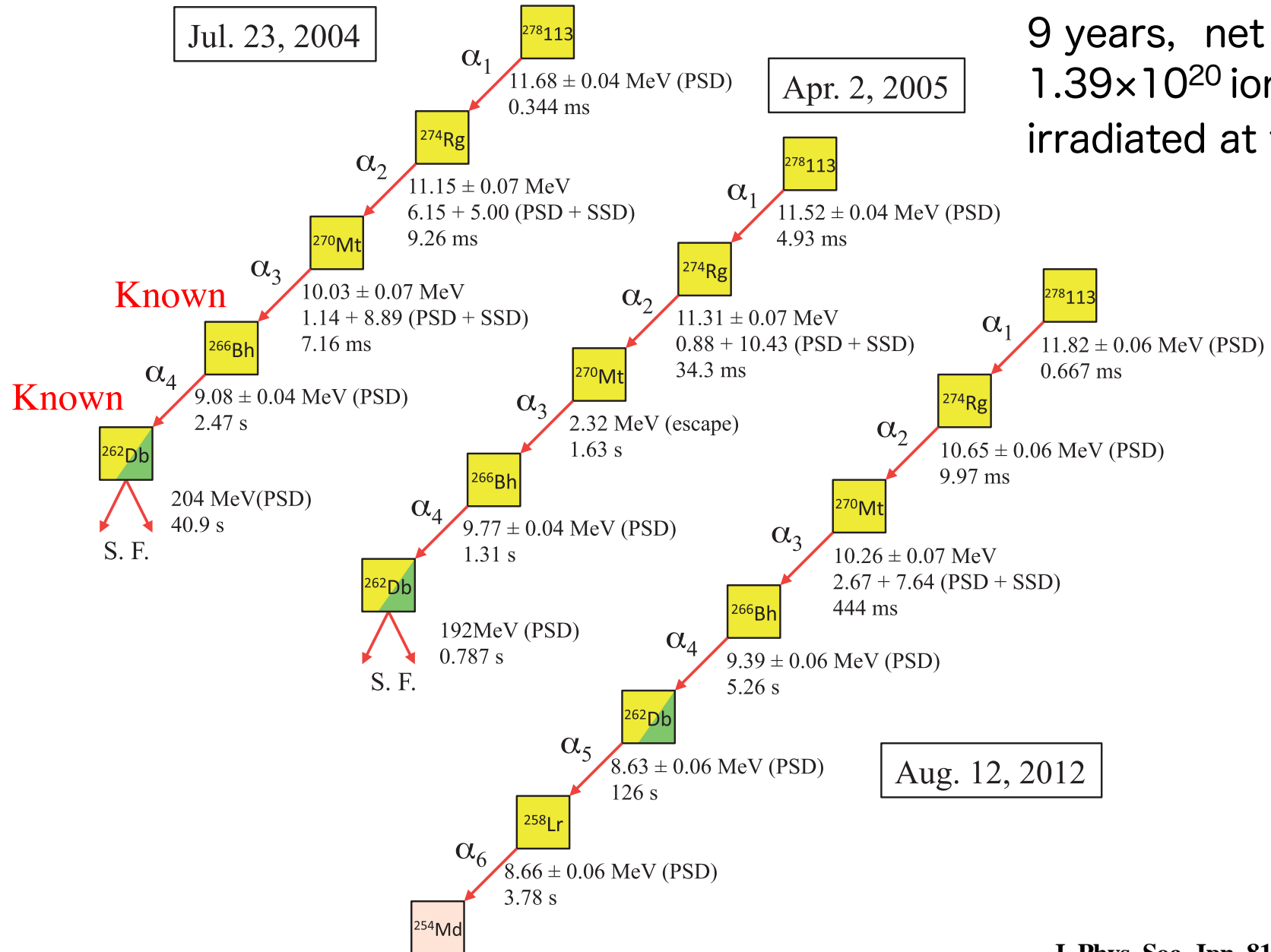
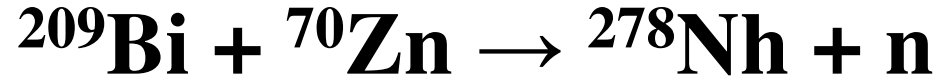
various charge states

independent on initial charge state

Progress in Particle and Nuclear Physics 62 (2009) 325-336

trajectory in magnetic field: $B \rho = 0.0227 \times \underline{A} \times (v/v_0) / \underline{q}$
 radius mass number charge

Element 113



9 years, net 574 days
1.39 × 10²⁰ ions were
irradiated at the target.

Irradiation Effects of Radiation

(1) Radiation trauma

lattice defect (metal, semiconductor)

(2) Ionization, Excitation, Radical production

dissociation and formation of chemical bond

oxidation-reduction, cross-link, polymerization

(3) Killing of organisms, Asexualization

sterilization, pest control, food irradiation,
radiotherapy

(4) Mutation

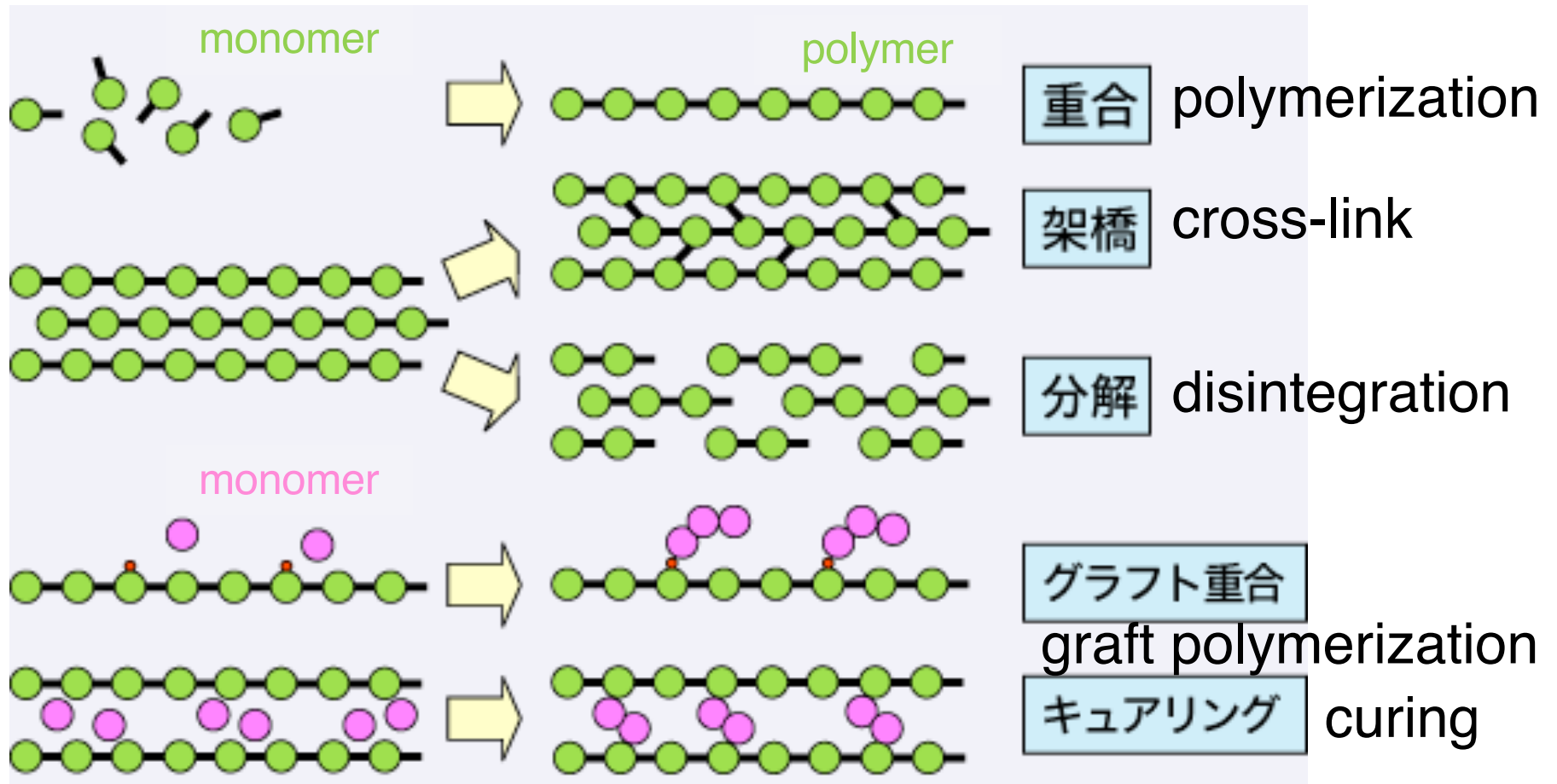
cereal → (e.g.) Reimei [rice]

fruit → (e.g.) Gold 20 century [pear]

flower → (e.g.) Kirari [carnation]



Reformulation and processing by radiation



- production of fluorine resin (PTFE) particles [radiolysis]
- radial tire, heat resistance electric wire, foam plastic [cross-linking]
- painting cement tile, laminate steel sheet, paper liner of adhesive label [radiation curing]

Prevention of melon fly

Kagoshima 鹿児島県

奄美群島 Amami islands
 昭和60年(1985) bebinig
 平成元年(1989) eradication

沖縄群島 Okinawa islands
 昭和61年(1986) bebinig
 平成2年(1990) eradication

久米島 Kume island
 昭和50年(1975) bebinig
 昭和53年(1978) eradication

宮古群島 Miyako islands
 昭和59年(1984) bebinig
 昭和62年(1987) eradication

八重山群島
 平成2年(1990) bebinig
 平成5年(1993) eradication

昭和49年(1974)

奄美群島

昭和48年(1973)

南北大東島
 昭和52年(1977)

昭和47年(1972)

昭和45年(1970)

沖縄県 Okinawa

宮古群島
 昭和4年(1929)

八重山群島
 大正8年(1919)

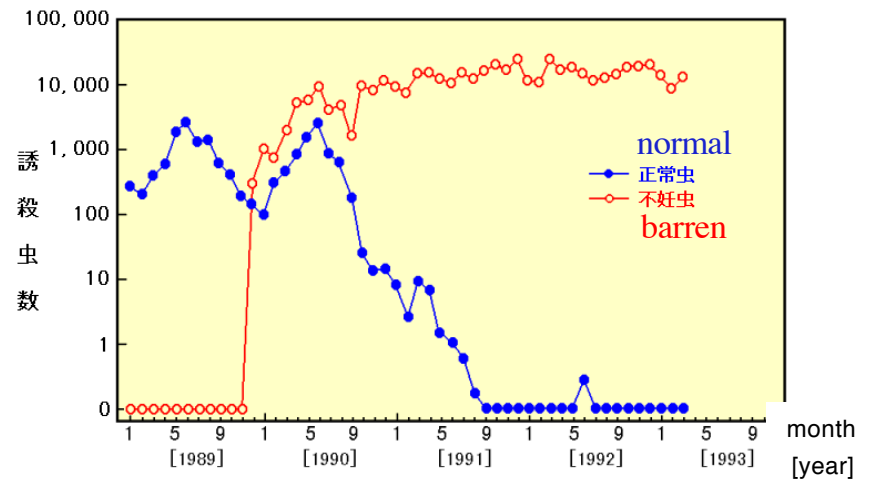
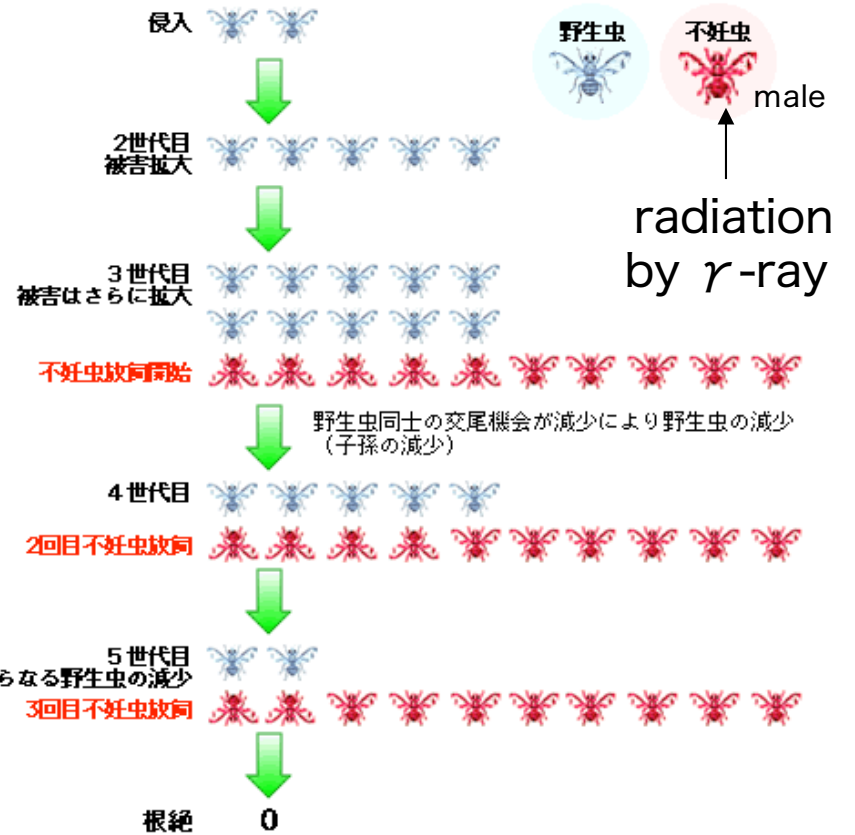


図3 八重山群島におけるウリミバエトラップ調査結果

[出典] 沖縄県農林水産部特殊病害虫対策本部: 平成4年 沖縄県特殊病害虫防除事業報告 第18号(1992年)p.24

<https://www.pref.okinawa.jp/mibae/index.html>
 (沖縄県病害虫防除技術センター)