Activation analysis

szerző: PGY

So what does a neutron cost?

Relative costs

Source	cost, $	flux	n / $
Reactors	1,000,000	10^{12}	10^{6}
CW	50,000	10^{8}	2000
Van de Graaff	200,000	10^{8}	500
Isotopes	>1000	10^{5}	100

So a reactor will produce the cheapest neutrons. However, it requires the greatest initial investment.

Activation Analysis

Methods where a measurable species is produced by nuclear bombardment and transformation.

Both quantitative and qualitative information can be obtained.

Species used for activation:

neutrons - about 90% of all publications
charged particles - p, d, t, and larger
photons - γ - limited application

Activation analysis

Neutron activation

Types

Fast	> 1MeV
Epithermal	< 1 MeV, > 0.026 eV
Thermal	@ 20°C, 0.026 eV, 2200 m/s

Principal reactions

Thermal	(n, γ)		
Fast	(n, p)	(n, 2n)	(n, α)
	(n, n')	(n, f)	

Charged particle and photon activation

Charged particle activation

protons (p, n) (p, 2n) (p, α) (p, d)

deuterons (d, p)

^{3}H and ^{4}He have also been used

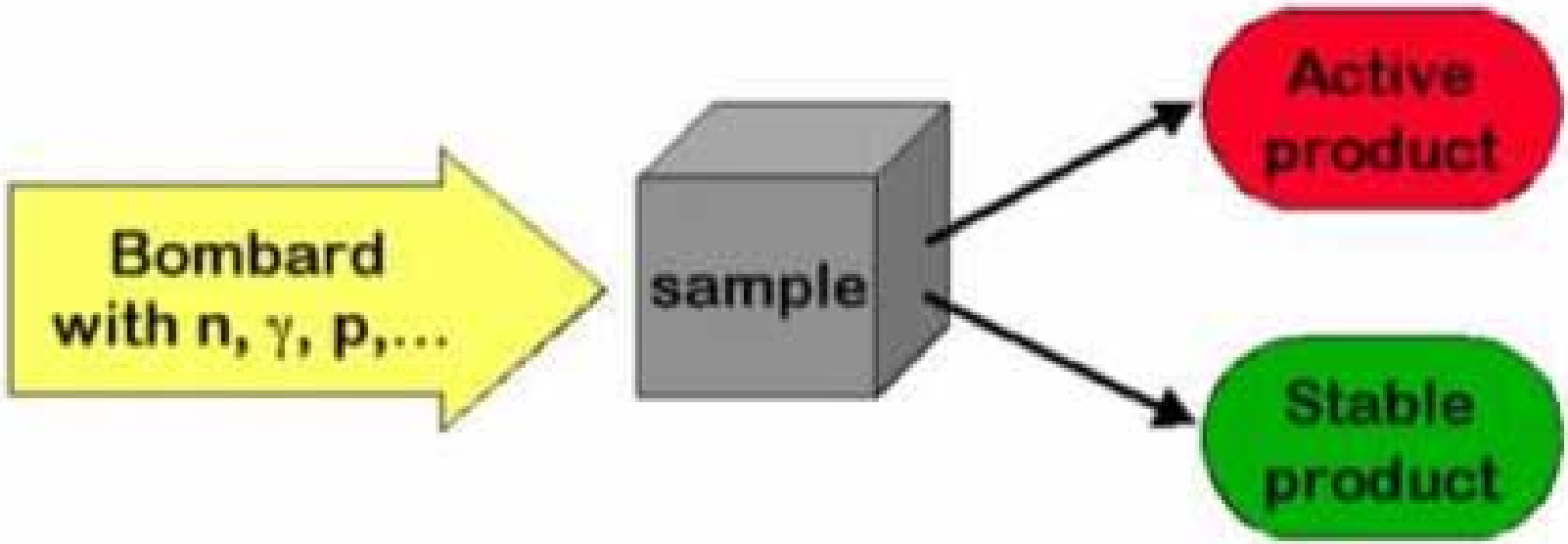
Photons (γ, n) (γ, p) (γ, γ')

(γ, γ') is the most common.

Thermal neutron activation (NAA) is the most commonly used.

Determining the effects of activation

When an activation occurs, one of two things can happen.



Formation of stable products

The number of product atoms produced can be predicted from:

$$N^* = N \phi \sigma t$$

Where

- N^* = the number of product atoms
- N = the number of target atoms
- ϕ = flux - for neutrons use units of n cm^{-2} s^{-1}
- σ = cross-section

Cross-section

This is a measure of the probability of the particular activation occurring.

It is given in units of barns

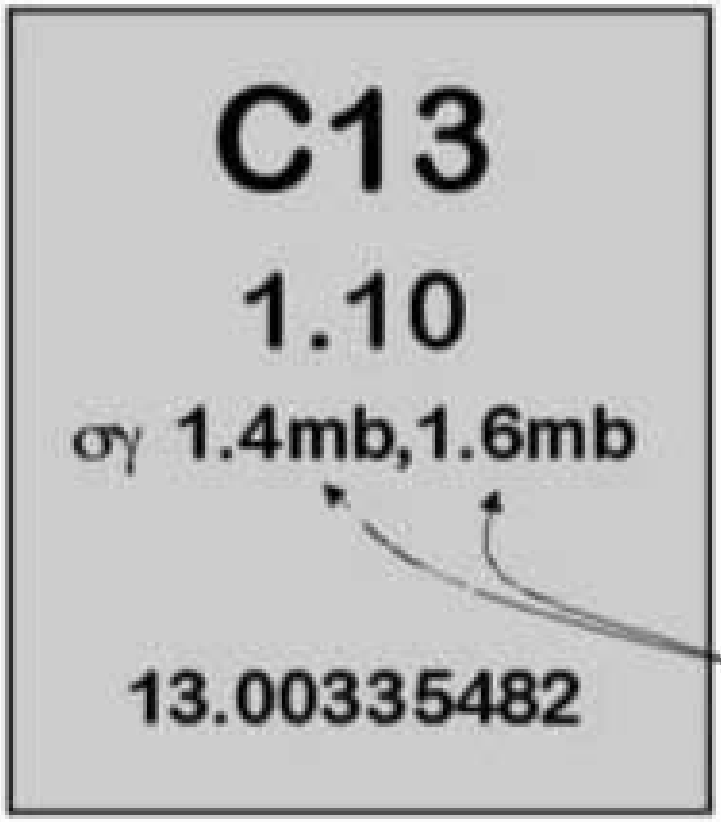
1 barn = 10^{-24} cm^2

Neutron cross-section information can obtained from:

The Barn Book

Chart of the Nuclides.

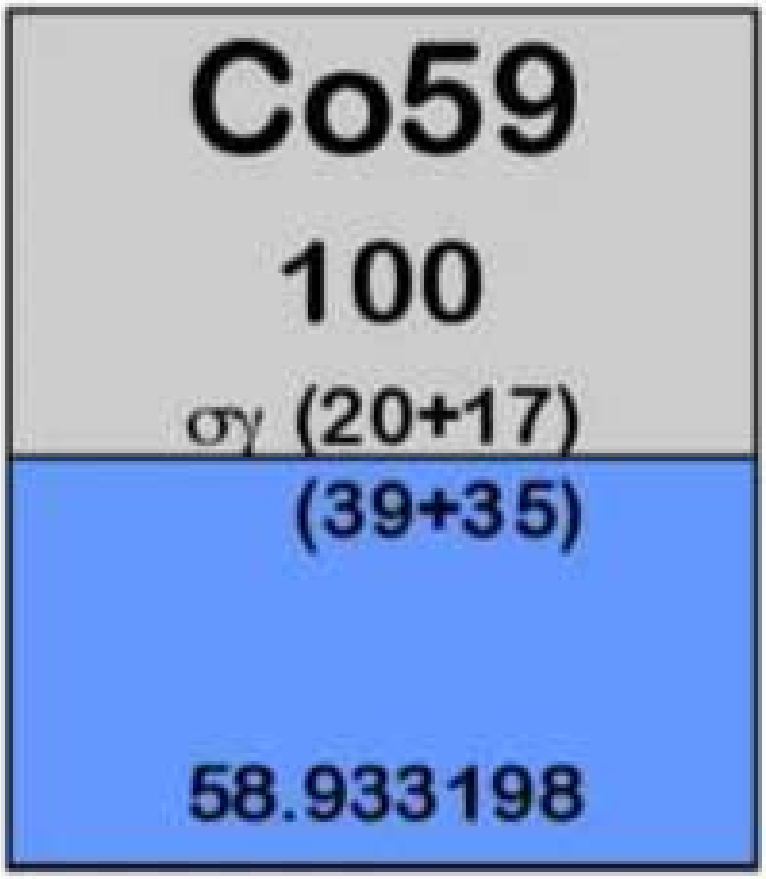
Cross-section information in the Chart of the Nuclides



While the information is not as extensive as that found in the Barn Book, it will be adequate for our purposes.

Thermal neutron and resonance integral cross-sections.

Cross section information in the Chart of the Nuclides



This example shows the thermal neutron cross-section for the (isomeric + first ground state)

followed by resonance integral cross-section leading to the (isomeric + 1st ground)

Neutron cross-sections

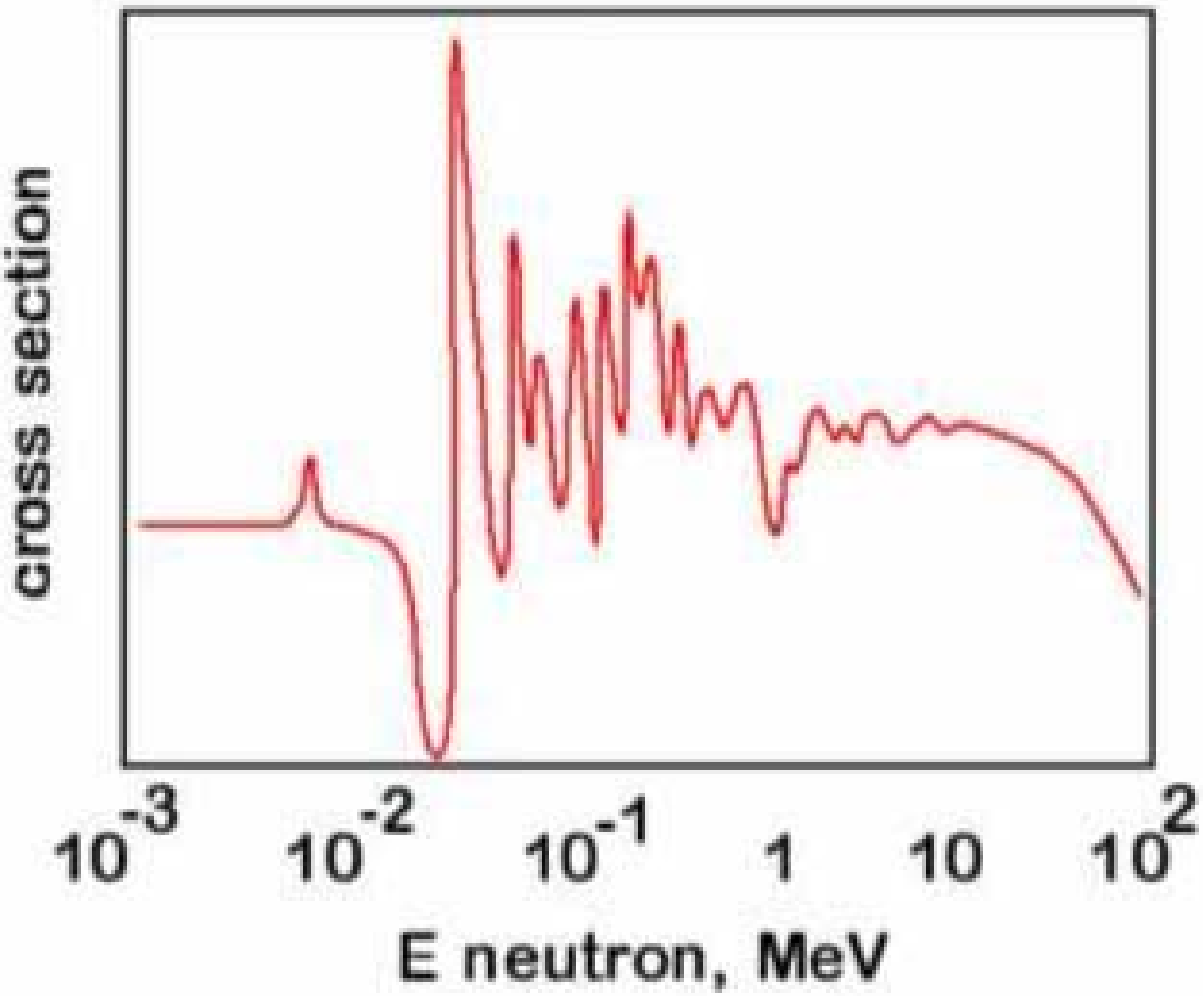
Values range from a few millibarns to several barns.

As the cross-section increases, the probability of a reaction occurring also increases.

Resonance cross-sections meet a quantum mechanical need of a nucleus.

This results in complex neutron absorption spectra.

Neutron cross-section for ^{27}Al



Formation of a stable product

Example $^{105}Pd\ (n, \gamma)\ ^{106}Pd$

For a one gram sample of palladium, determine the percent of ^{105}Pd converted to ^{106}Pd if:

Activation time = 1 hour

$\phi\ n_{th}$ = 1×10^{12} n $cm^{-2}\ s^{-1}$

σ = 22 barns

Formation of a stable product

$$N^* = N \phi \sigma t$$

First, you need the number of target atoms.

1 gram Pd contains 0.2233 g ^{105}Pd

(abundance is obtained from the Chart)

$mol_{Pd\text{-}105}$ = 0.2233 g / 105 g/$mol_{Pd\text{-}105}$

= 2.13×10^{-3} mol

$Atoms_{Pd\text{-}105}$ = 2.13×10^{-3} mol x 6.022×10^{23}

= 1.28×10^{21} atoms

Formation of a stable product

$$N^* = N \phi \sigma t$$

Now, convert the cross-section from barns to cm^2 (1 barn = 10^{-24} cm^2)

Thermal neutron cross-section

22 barns = 2.2×10^{-23} cm^2

Finally, convert the activation time to seconds: 1 hour = 3600 seconds.

Formation of a stable product

$$N^* = N \phi \sigma t$$

Now, we're ready to calculate:

$N^* =$ $(1.28 \times 10^{21}$ atoms)

$\times (1 \times 10^{12}$ n cm^{-2} $s^{-1})$

$\times (2.2 \times 10^{-23}$ $cm^2)$

$\times$ (3600 seconds)

1.01×10^{14}

Formation of a stable product

While a very large number of ^{106}Pd are formed, only a small percentage of the ^{105}Pd has been converted.

$$\% \text{ conversion} = 100\ (1.01 \times 10^{14}/1.28 \times 10^{21})$$
$$= 7.89 \times 10^{-6}\ \%$$

(about 1 in every 10 million)

Actual activation may be slightly greater due to resonance neutrons. In this case the cross-section would be 100 barns

Formation of a stable product

So, what is is good for?

Our product is stable and naturally found in our sample.

We only made a trace amount of it

What can we measure?

Prompt Gammas

Prompt gammas

When a target nucleus is bombarded with a thermal neutron, a prompt or capture gamma is produced.

$$^{A}X\ (n, \gamma)\ ^{A+1}X$$

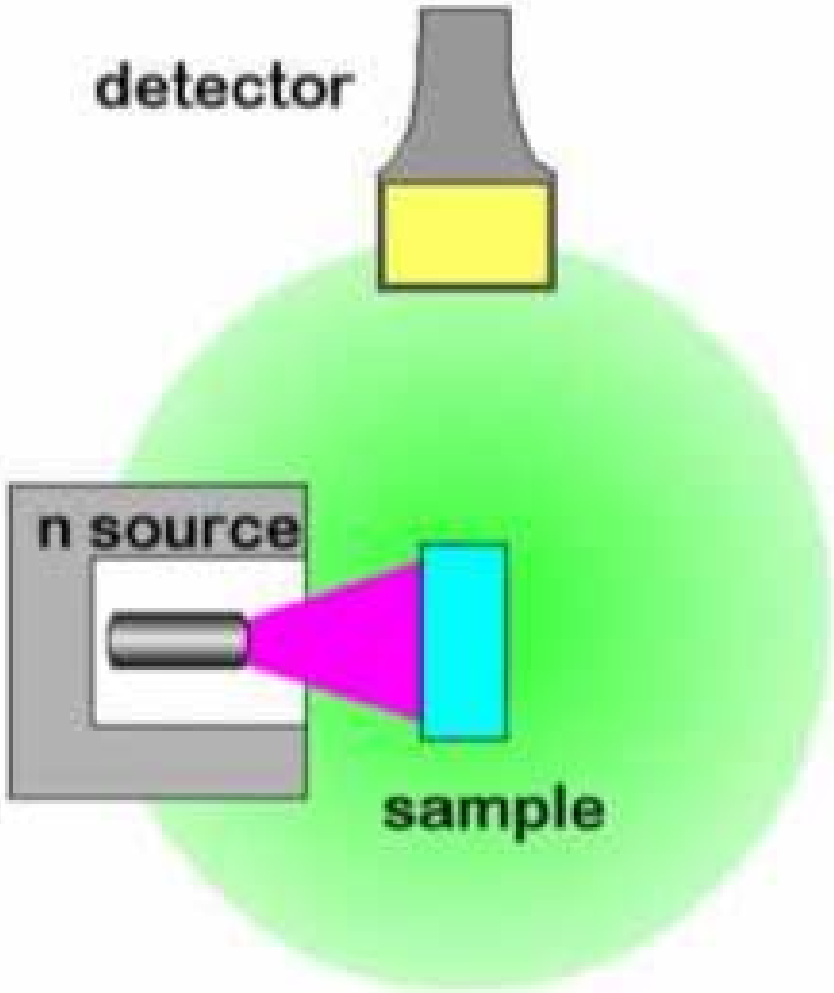
The energy range for this γ is 2-12 MeV

Due to resonance neutron absorption, the γ spectra can be very complex.

All (n, γ) produce prompt gamma.

When a stable product is formed, this is all we can measure.

Measuring prompt gammas



The detector must be at an off angle and shielded.

If not, you will end up activating the detector.

Presence of Na, I, Tl and Al prompt γ are a good sign that you have a poor setup.

Formation of unstable products

We must account for the fact that unstable products will begin to decay as soon as they are produced.

As activation time increases, the amount of our unstable product increases, as does its rate of decay.

We must be able to account for this.

Formation of unstable products

$$\frac{dN^*}{dt} = N \phi \sigma (-\lambda N^*)$$

$$\lambda N^* = \text{activity} = N \phi \sigma \left(1 - e^{-\frac{0.693\, t_i}{t_{1/2}}} \right)$$

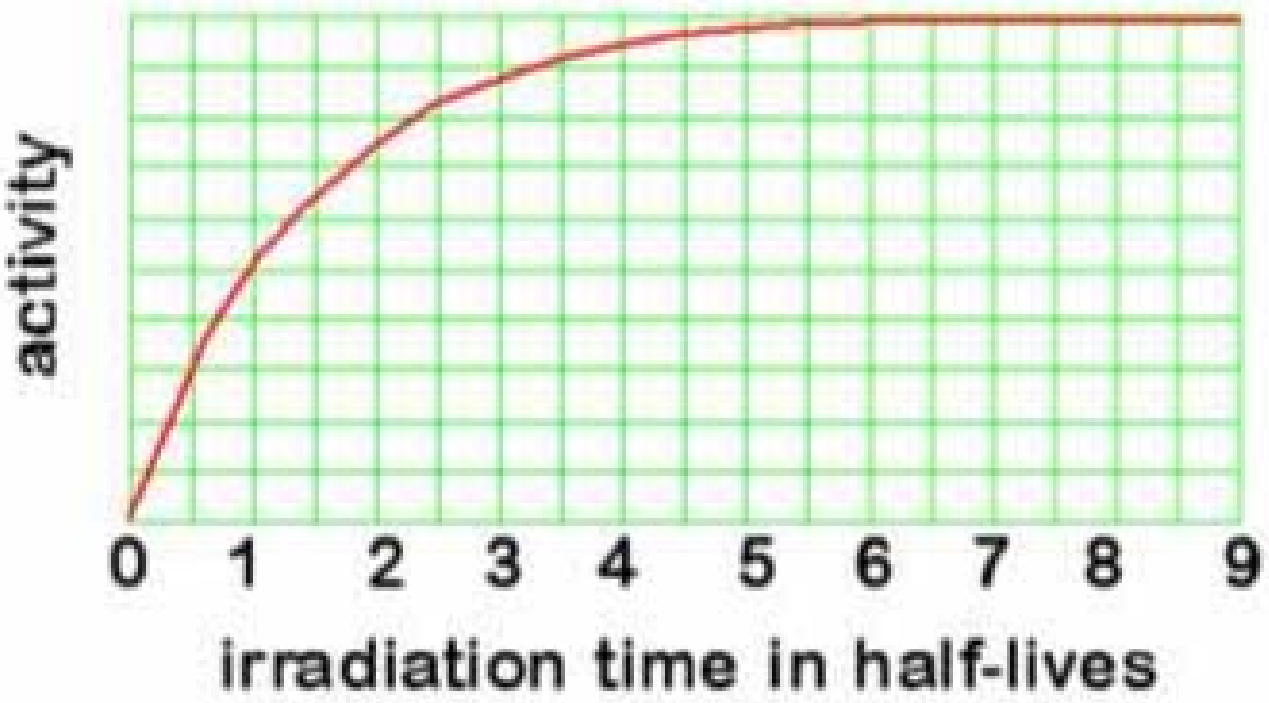
saturation factor

t_i - irradiation time
$t_{1/2}$ - half-life of product

These only need to be in the same units.

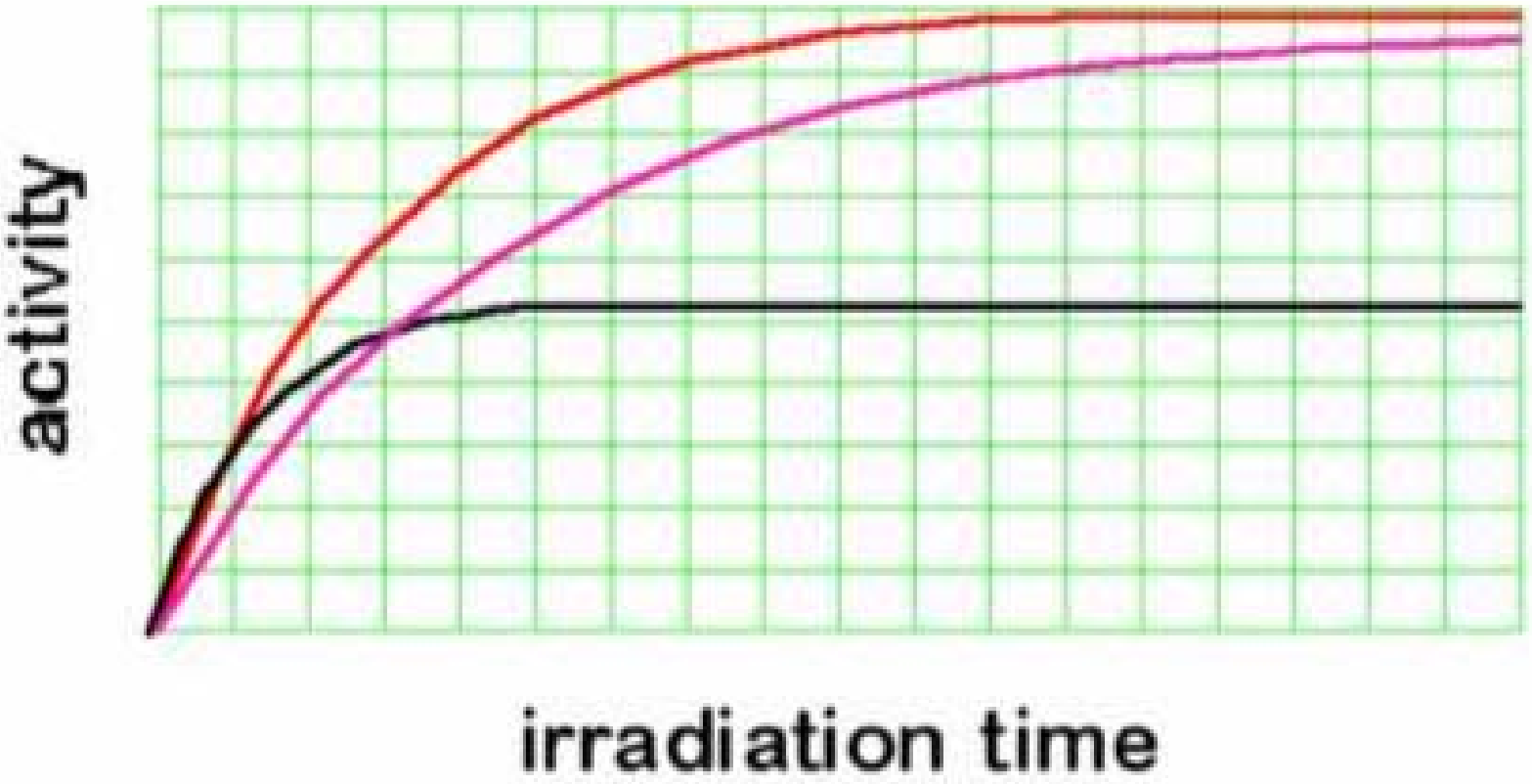
Formation of unstable products

While activity will initially increase rapidly, a maximum is reached within 7 half-lives.



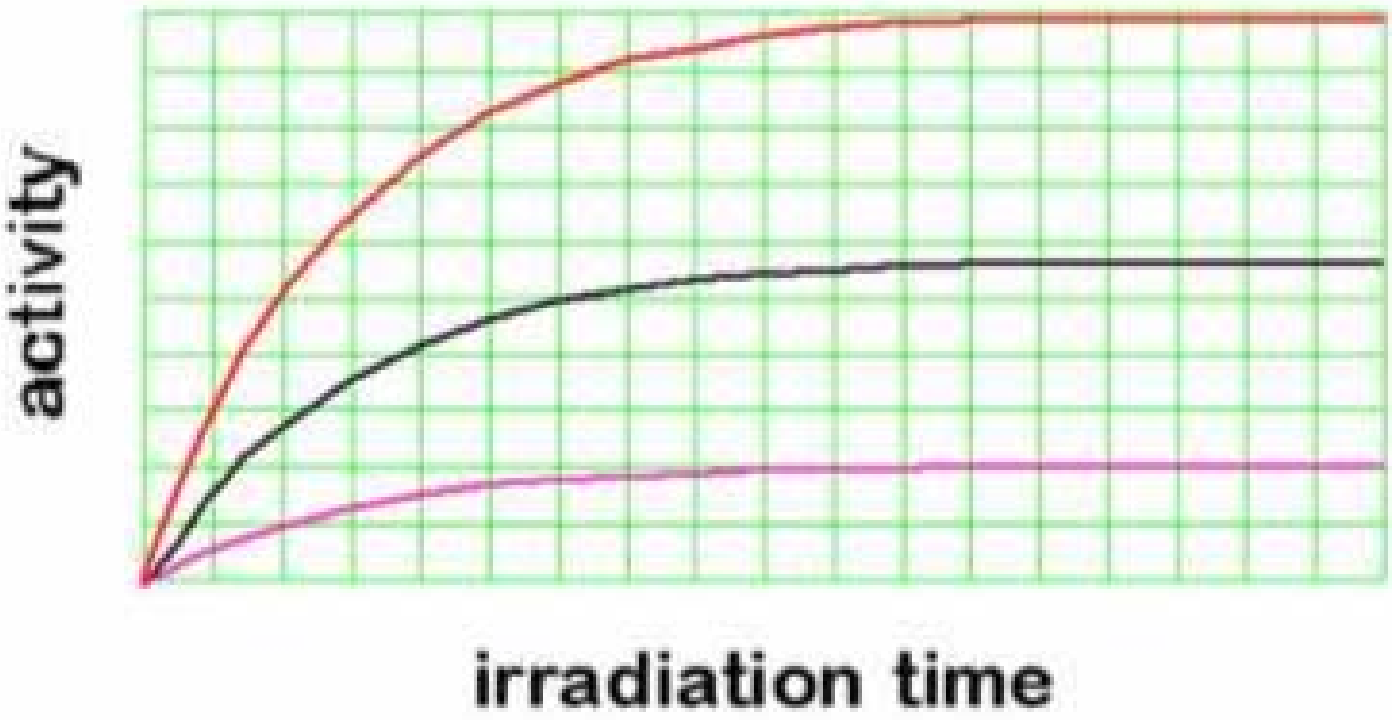
Formation of unstable products

When several nuclides are present, each will reach a maximum at a different time



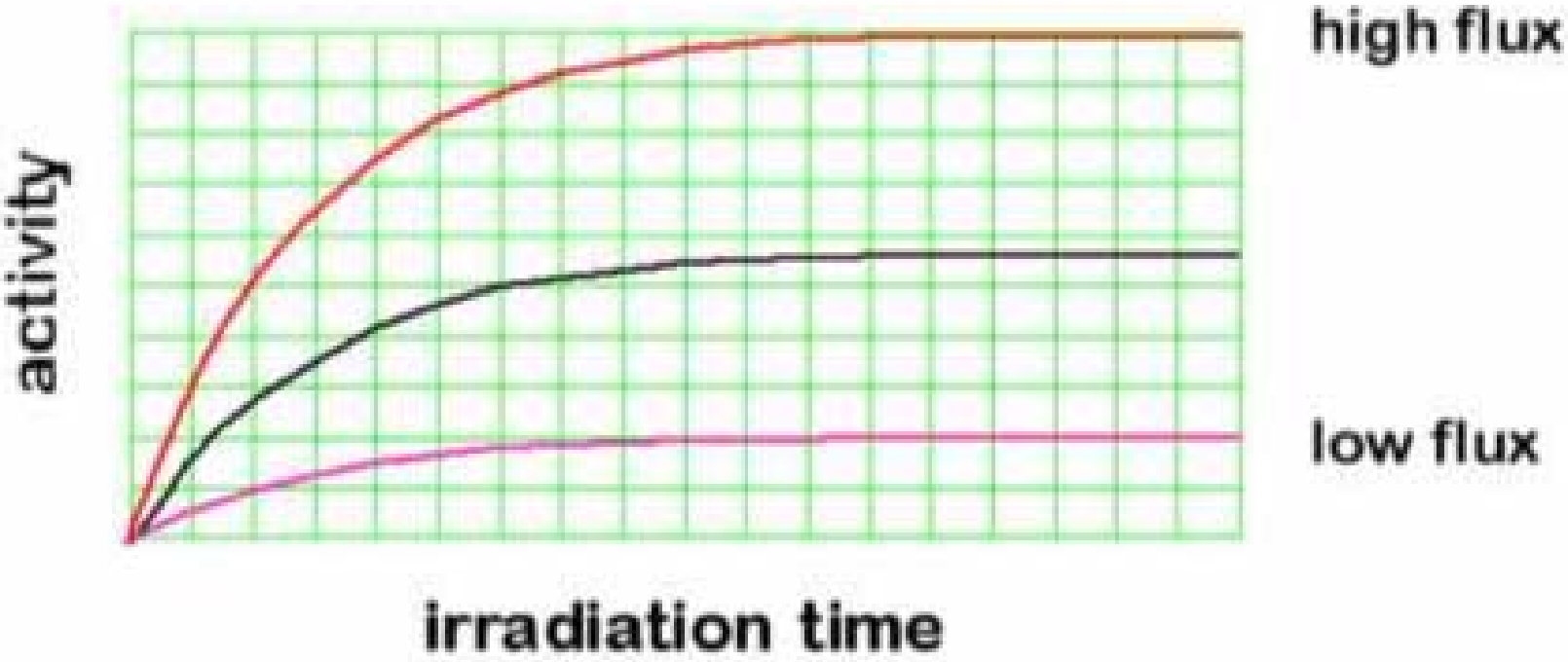
Formation of unstable products

For samples of the same nuclide, the activity produced will be proportional to concentration.



Formation of unstable products

Finally, higher neutron fluxes will result in higher activities being produced.



Formation of unstable products

For each element, you must consider

The stable isotopes being activated

cross-section & percent abundance

For the unstable product

half-life, determines the time required for maximum activation

Neutron source flux

This factor also determines the maximum activity produced.

Unstable product activation

Example.

Determine the activity of ^{65}Ni produced by irradiation of one gram of a nickel sample for 24 hours. Flux = 10^{12} n $cm^{-2}s^{-1}$

The following was obtained from the Chart.

^{64}Ni

abundance = 0.91%

At. Wt. = 63.928

σ_γ = 1.55 barns

65Ni

$t_{1/2}$ = 2.52 h

Unstable product activation

$$\lambda N^* = \text{activity} = N \phi \sigma \left(1 - e^{- \frac{0.693\, t_i}{t_{1/2}}} \right)$$

$N = (6.022 \times 10^{23})\ (0.0091\text{g}) / (63.927\ \text{g/mol})$

$= 8.57 \times 10^{19}$ atoms ^{64}Ni

$\phi = 10^{12}\ \text{n cm}^{-2}\text{s}^{-1}$

$\sigma = 1.55$ barns $= 1.55 \times 10^{-24}\ \text{cm}^2$

$t_i = 24$ hours $\quad t_{1/2} = 2.54$ hours

Unstable product activation

$$\text{activity} = (8.57\times10^{19})(10^{12})(1.55\times10^{-24})\left(1 - e^{-\frac{.693(24h)}{(2.54h)}}\right)$$

$$\text{Activity} = 1.32 \times 10^{8} \text{ dps}$$

$$= 2.21 \times 10^{6} \text{ dpm}$$

Qualitative Analysis

γ spectroscopy is most often used.

Many species will emit only a single major gamma ray. Example. ^{109}Cd - 88 keV

Other species will emit a characteristic set of gamma rays.

Many gamma will overlap - dependent on detector type and system resolution.

Some γ, like 0.511 MeV are relative common and non-specific.

Qualitative Analysis

Most samples are mixtures

- Different elements
- Different isotopes of the same element.

All are activated at the same time so you need to consider following for all possible elements and isotopes.

- Abundance and cross-section
- half-life and emission mode of products.

This may help prevent 'unexpected' results.

Qualitative Analysis

What would you expect for the activation of a pure $CuSO_4$ sample?

Copper	%	σ	$t_{1/2\ product}$	γ
^{63}Cu	69.17	4.47	12.701h	1.346
^{65}Cu	30.83	2.17	5.10m	1.039
Sulfur				
^{34}S	4.21	0.23	87.2d	no γ
^{36}S	0.02	0.23	5.05m	1.75

Qualitative Analysis

Sulfur	%	σ	$t_{1/2\ product}$	γ
^{32}S	95.02	0.53	stable product	
^{33}S	0.75	0.45mb	stable product	
^{34}S	4.21	0.23	87.2d	no γ
^{36}S	0.02	0.23	5.05m	1.75

Qualitative Analysis

Oxygen	%	σ	$t_{1/2\ product}$	γ
^{16}O	99.762	.19mb	stable product	
^{17}O	0.038	0.4mb	stable product	
^{18}O	0.200	0.16mb	26.9s	0.197
				1.357
				0.110

Qualitative Analysis

This problem can become much worse for some elements.

Consider cadmium

Exists as 8 stable isotopes

Upon activation, 8 active species can be produced - including 4metastable states.

There are a few steps that can be taken to help in your analysis.

Qualitative Analysis

If sensitivity is not a problem, use a Ge(Li) or intrinsic Ge detector. Most γ can be identified if the resolution is high enough.

Be creative with your activation time.

Short half-live products will be produced more rapidly than long half-life species.

Little of the 'long half-life' species will be produced.

Qualitative Analysis

Introducing a 'hold' time.

- Short half-life species can also introduce a problem.
- Gamma from these species can be reduced or eliminated if you wait a fixed period of time before counting and allowing them to decay away.
- The time period should be fixed if you plan on doing any quantitative analysis.

Qualitative Analysis

Fast neutrons.

Thermal neutron sources always contain at least a few 'fast' neutrons.

This can cause some unexpected problems - a reaction other than (n,γ)

Example

$^{23}Na\ (n, \gamma)\ ^{24}Na$

$^{24}Mg\ (n, p)\ ^{24}Na$

(fast neutron activation)

Qualitative analysis

Fast neutrons.

If such problems are possible, you can deal with them.

Wrapping your sample in Cd or B will remove most thermal neutrons.

If there is a significant difference in wrapped and unwrapped samples, then fast neutrons are a likely source.

Quantitative analysis

Absolute method.

Determination of N from the activity.

Seldom used because:

Detector efficiency must be know exactly for the specific γ being measured.

Cross-section values are only an estimate or average. They can vary by $\pm$ 50%.

Quantitative analysis

Getting even a good estimate as to the flux is hard to do. It will also typically change with time.

- Requires the use of a VP grade element of exactly the same geometry.

Neutron source is not monochromatic.

- You obtain an energy range
- The range can vary.

Quantitative analysis

Relative Method.

This is the typical approach to use.

$$\frac{A_{unknown}}{A_{standard}} = \frac{N_{unknown}}{N_{standard}}$$

Single point calibration will give adequate results.

Quantitative analysis

Relative Method.

As with most analytical methods, you must treat your sample and standard identically.

Activation time, source and position

Identical counting conditions

The same type of sample container

As similar a matrix as is possible.

Accuracies of $\pm$0.1% are possible but $\pm$2% are typically observed.

Neutron sources.

To do NAA, you got to have neutrons.

They can be produced using

Nuclear reactors

Isotopic sources

Particle accelerators

Each has its own limits and advantages.

Nuclear reactors - research type

These rely on ^{235}U enrich fuel (3-6%).

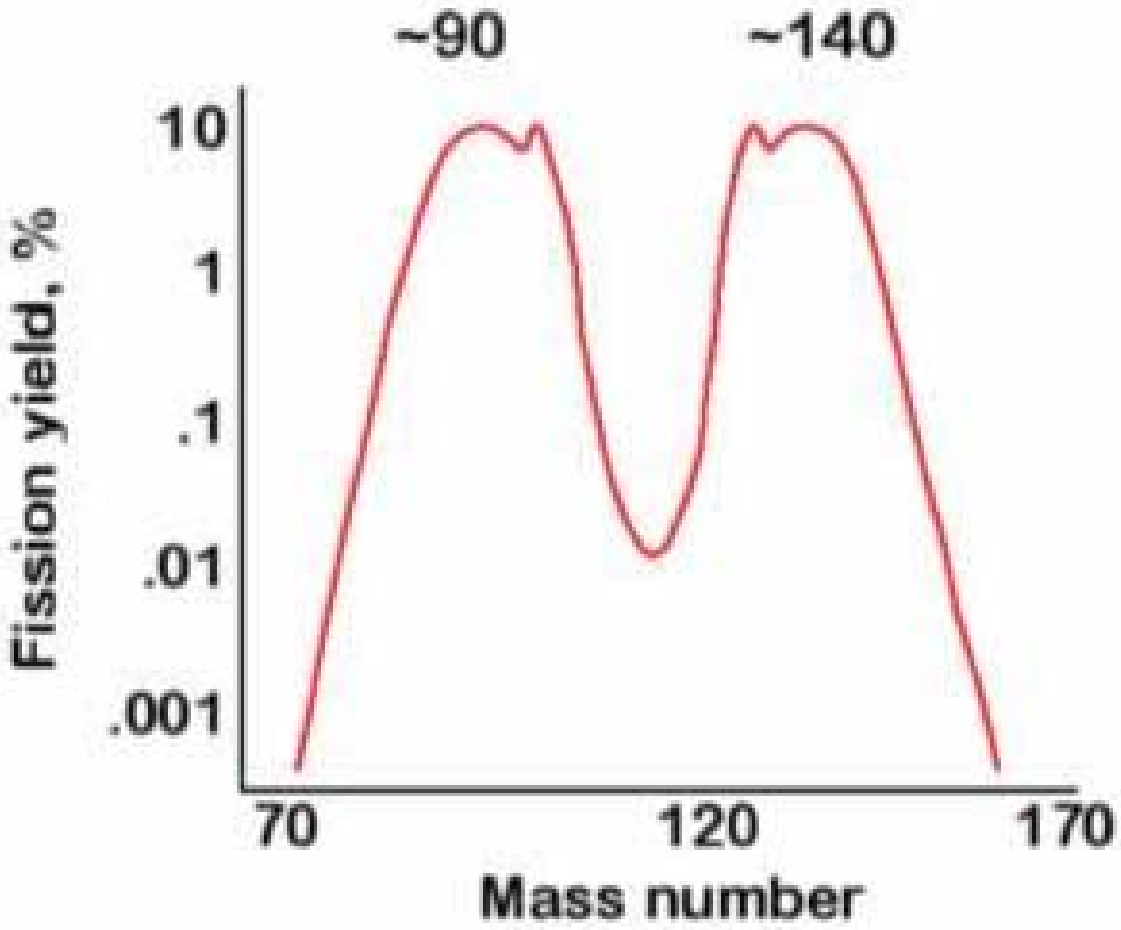
Neutrons are produced via:

$^{235}U + n_{th} \rightarrow 2\ ff + \sim 2.5\ n + \sim 200\ MeV$

ff - fission fragments.

The actual fragments occur over a distribution - Mae West Curve.

Mae West Curve



These fragments are also the major source for the tracers one can obtain.

Reactor flux

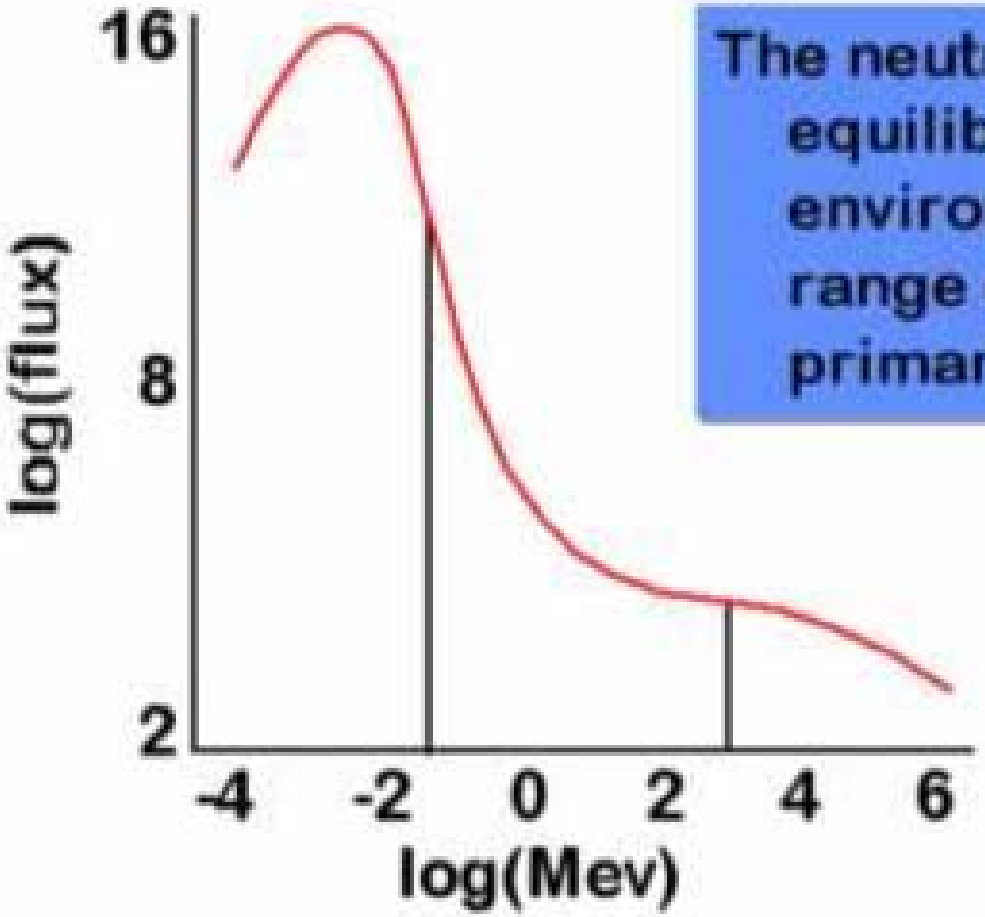
Reactors will have a flux of 10^{11}-10^{15}.

A few 'pulsed' type reactors can achieve values of 10^{17}-10^{21}.

Neutrons are initially moving very fast because the get most of the energy.

$$M_n = \frac{M_{\text{other particle}}}{\text{mass}_n + \text{mass}_{\text{other}}}$$

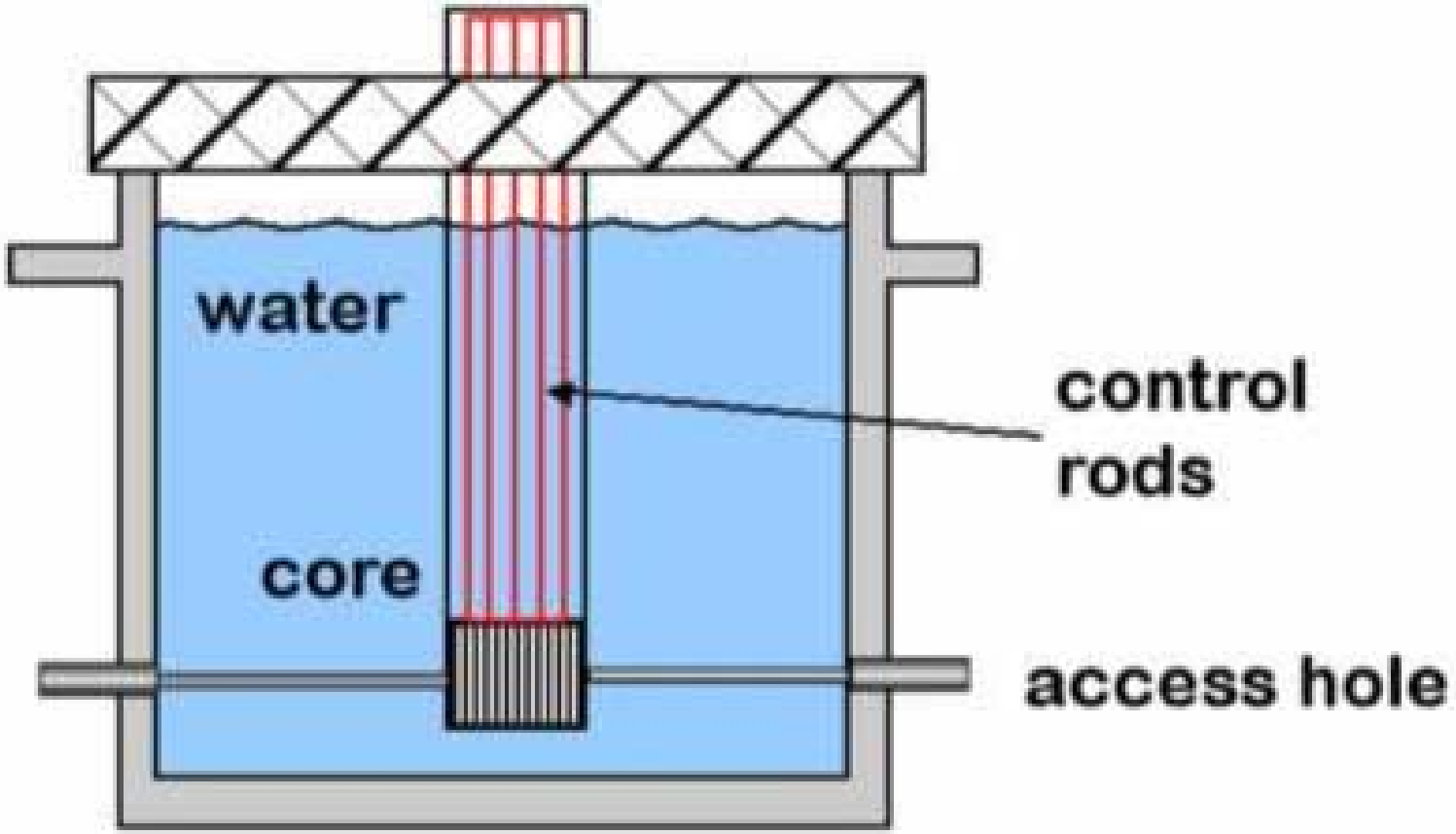
Reactor flux



The neutrons will rapidly equilibrate with their environment, producing a range of energies - primarily thermal.

Research reactor

'Swimming Pool' type



Moderators

Most ^{235}U reactors use H_2O or D_2O as a moderator.

Light water reactors

Water is used to slow the neutrons and to dissipate heat.

Heavy water reactors

Added benefit of not needing to enrich the fuel. D_2O does not absorb the neutrons. Will also produce n via d(γ,n)H reaction.

Control rods

Use elements at absorb neutrons - each has a large cross-section

^{10}B	-	3838
^{111}Cd	-	24
Gd	-	80 to 255000 (based on isotope)

These are typically produced as alloys.

Pulsed reactor

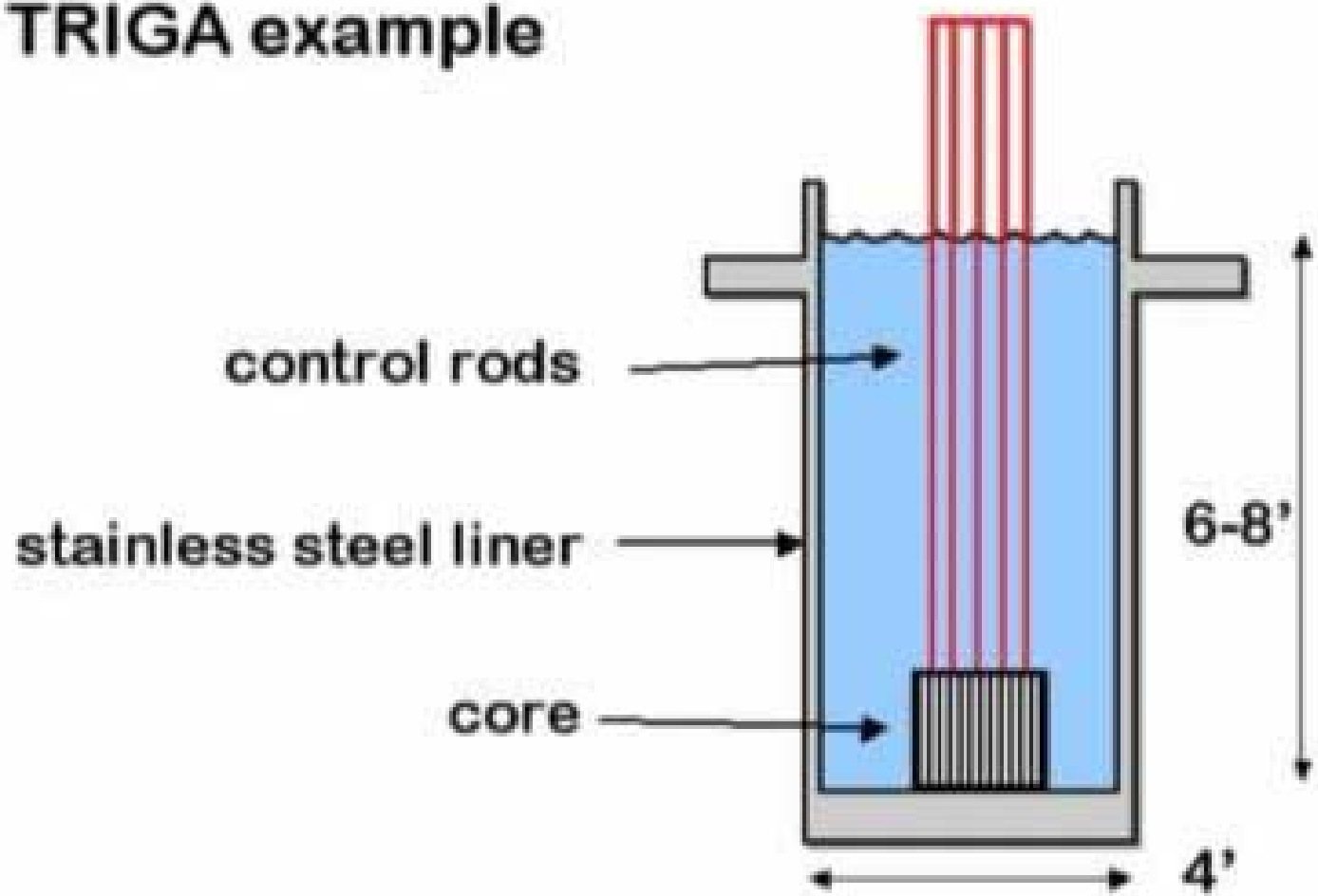
These include the TRIGA, Slow Poke and Pulstar types.

They rely on using Uranium hydride as the fuel. It also acts as a moderator.

Once the fuel rods are removed, it can produce very high fluxes but can't go critical

Pulsed reactor

TRIGA example



Isotopic sources

$^{9}Be\ (\gamma, n)\ ^{8m}Be$

Be is put in a mixture with a γ emitter.

γ energy must be at least 1.6 MeV.

^{24}Na is usually used for this purpose

It produces a 2.75 MeV gamma.

Source will produce a flux of - 10^{5} n $cm^{-2}s^{-1}$ per Ci of ^{24}Na.

Because of the g produced, this source requires a lot of shielding.

Isotopic sources

$^{9}Be\ (\alpha,n)\ ^{12}C$

Neutrons can also be produced if ^{9}Be is put in contact with an alpha emitter.

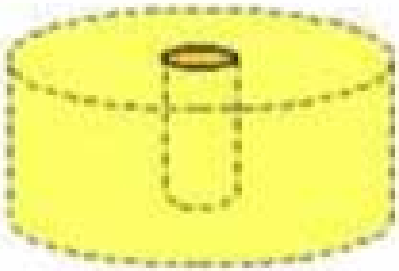
Less shielding is required.

Most common type is a Pu(Be) source.

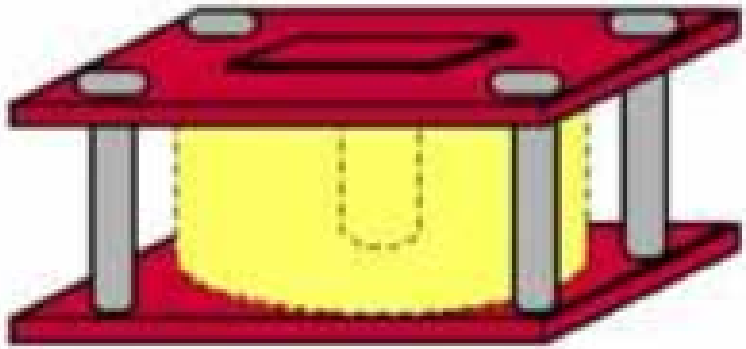
Both metals can be powdered and sealed in wax producing a 'portable' source.

Isotopic sources

Pu(Be) source



Wax mounted Pu and Be powders with a bore.



Complete mounting with lid that can and should be locked down when the source is not in use.

Isotopic sources

Pu(Be) sources.

Will produce a flux of 10^6 n $cm^{-2}s^{-1}$ for each Ci of plutonium.

Long life source due to half-life of Pu.

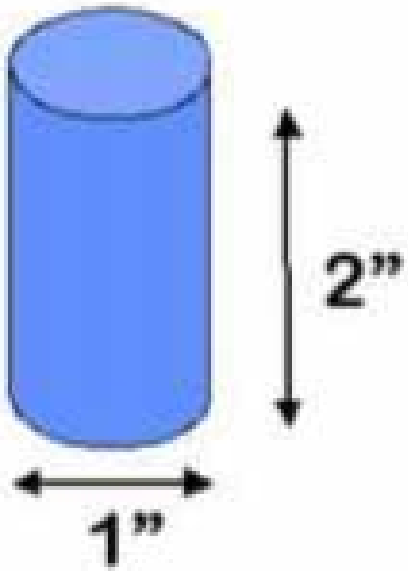
U.S. citizens can not own Pu. However, the sources can be leased from the government.

Isotopic sources

ABC source

A mixture of americium, beryllium & curium.
First and last are alpha emitters.

It can produce a flux
of 10^5 / Ci



Isotopic sources

^{252}Cf - man made element

This isotope will spontaneously emit neutrons at high flux.

Comes close to being a point source of neutrons.

$t_{1/2}$ = 2.6 years.

1/8" x 1.5"

This is a very expensive source costing over $10 / microgram.

Isotopic sources

^{252}Cf

1 mg can produce a flux of 106.

Since the source so small, several of them can be placed around a sample.

Also, the source can be surrounded with uranium to amplify the flux.

- can achieve 10^{11}
- close to a reactor flux

Particle accelerators

Cockcroft-Walton

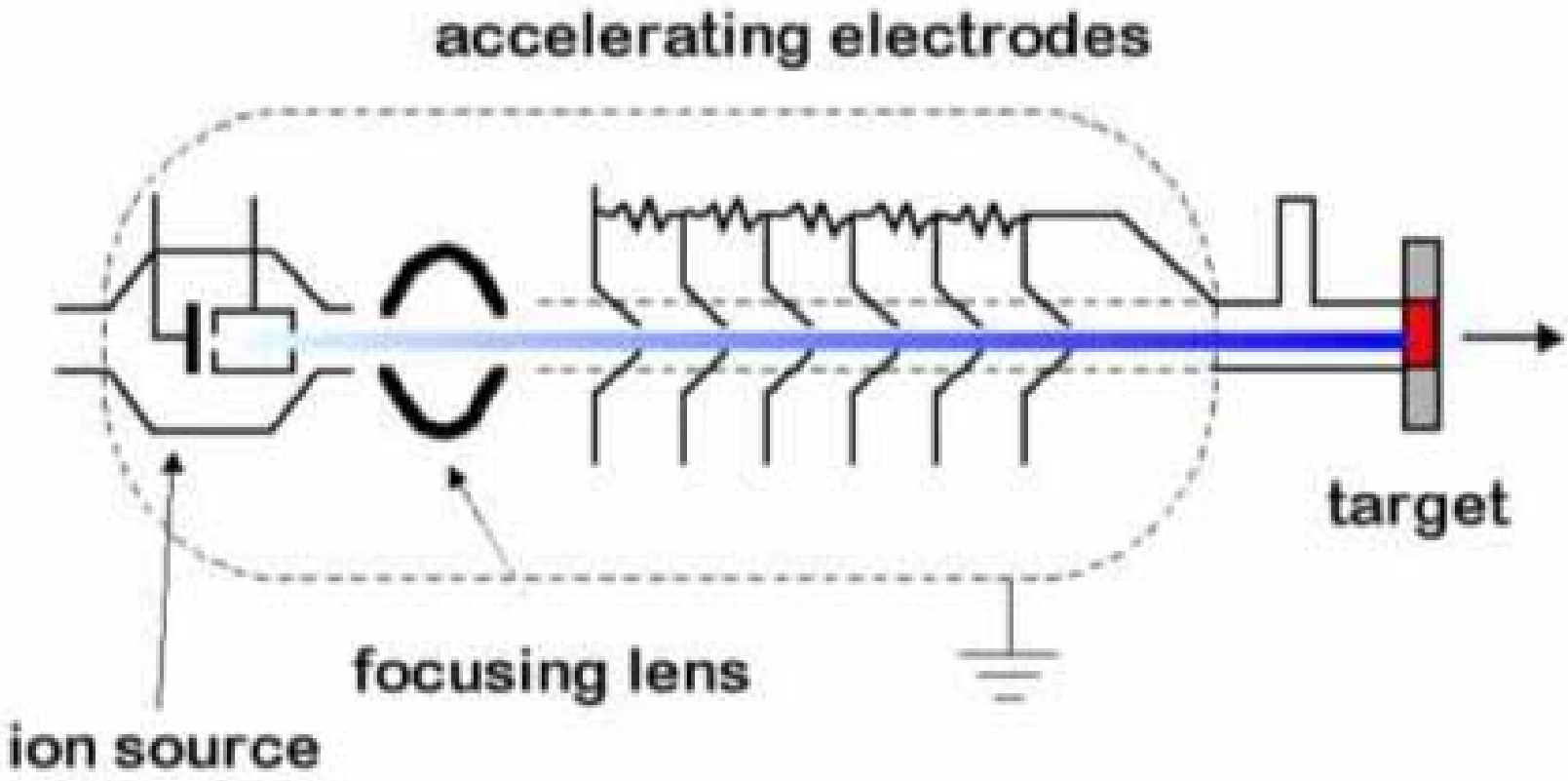
First accelerator

Made with spare parts that mysteriously disappeared from around their physics department - Graduate Students in action.

Uses a voltage doubling circuit that converts 110V to 100,000 V.

Capacitors are charged in parallel then discharged in series.

Cockcroft-Walton accelerator



Cockcroft-Walton accelerator

The accelerator will produce a stream of fast moving ions (p, d, α, ...) that then bombard a target.

Example reactions

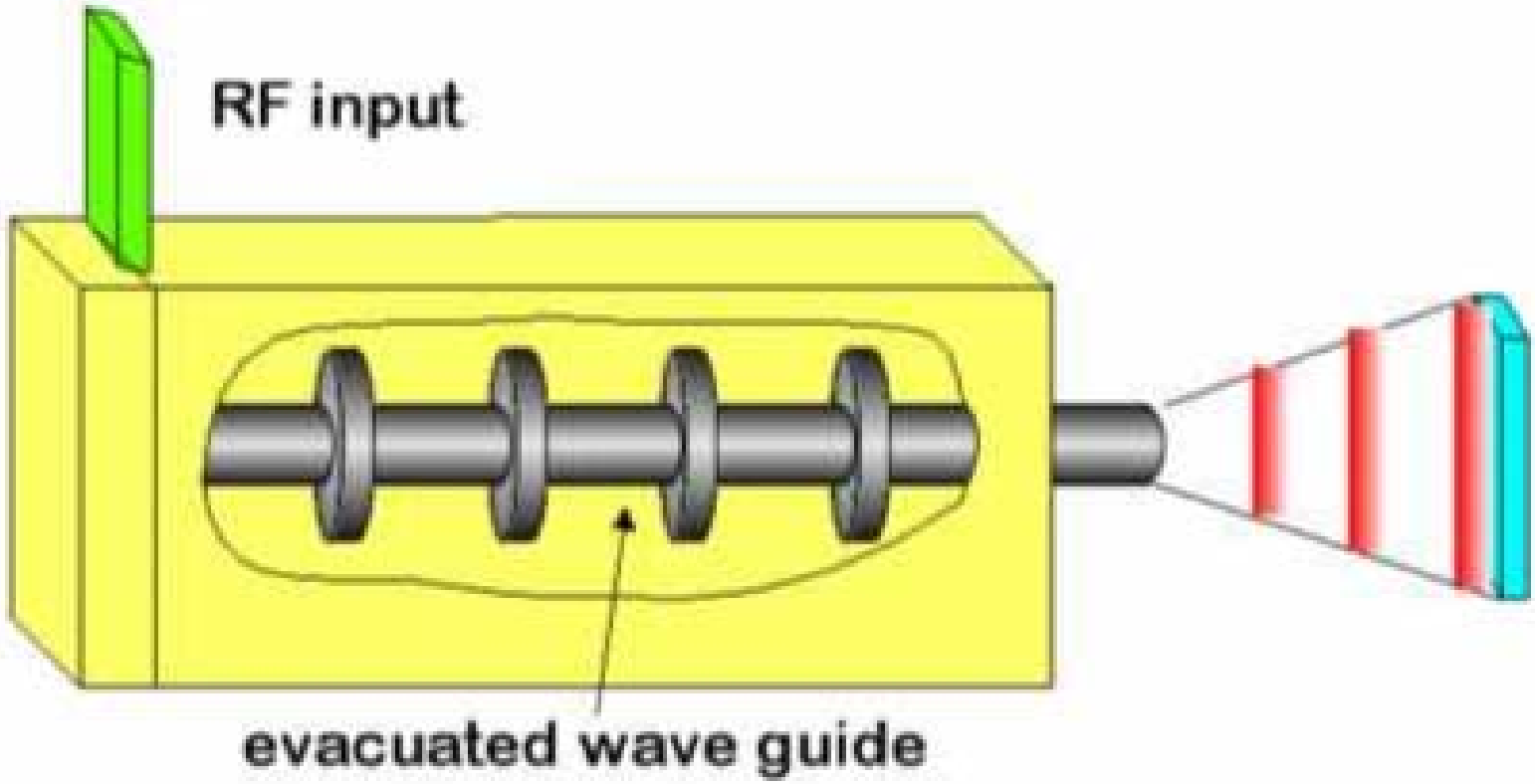
$^{2}H(d, n)\ ^{3}He$ 2.3 MeV neutrons

$^{3}H(d, n)\ ^{4}He$ 14.6 MeV neutrons

Deuterium is absorbed into the target metal and the other particle is 'fired' at it.

Linear accelerators

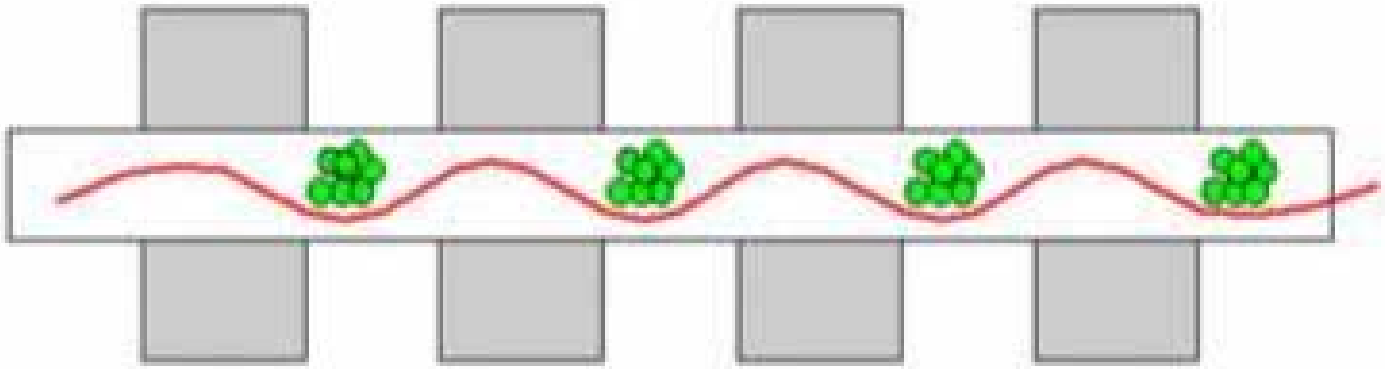
Either a voltage gradient or a 'kick' is given at specific points.



Linear accelerators

The accelerated particles are produced as 'bunches' based on the applied RF.

Since linear accelerators can be VERY long, enormous energies can be produced.



Van de Graaff generators

Huge electrostatic potentials can be developed- 2×10^6 V.

These generators can also run in tandem with a CW accelerator to produce potentials over 10^7 V.