Time scale of radioactive clock

$(t_{1/2})$ determines its range of application: history (2000 y), archaeology (10 000 y), anthropology (100000 y), evolution >10 My, geology (100 My), cosmology (10Gy)

<table>
<thead>
<tr>
<th>Radioactive Parent</th>
<th>half-life (y)</th>
<th>Stable Daughter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium 40</td>
<td>$1.3\cdot10^9$</td>
<td>Argon 40</td>
</tr>
<tr>
<td>Rubidium 87</td>
<td>$4.8\cdot10^{10}$</td>
<td>Strontium 87</td>
</tr>
<tr>
<td>Thorium 232</td>
<td>$1.4\cdot10^{10}$</td>
<td>Lead 208</td>
</tr>
<tr>
<td>Uranium 235</td>
<td>$7.04\cdot10^8$</td>
<td>Lead 207</td>
</tr>
<tr>
<td>Uranium 238</td>
<td>$4.46\cdot10^9$</td>
<td>Lead 206</td>
</tr>
<tr>
<td>Chlorine 36</td>
<td>$3.0\cdot10^5$</td>
<td>Argon 36</td>
</tr>
<tr>
<td>Aluminum 26</td>
<td>$7.16\cdot10^5$</td>
<td>Magnesium 26</td>
</tr>
<tr>
<td>Carbon 14</td>
<td>5730</td>
<td>Nitrogen 14</td>
</tr>
</tbody>
</table>
Review of the Radioactive Decay Law

decay of a radioactive substance with decay constant: \( \lambda = \ln 2 / t_{1/2} \)

\[
\frac{dN}{dt} = -\lambda \cdot N \\
\frac{dN}{N} = -\lambda \cdot dt
\]

\[ N(t) = N(t_0) \cdot e^{-\lambda \cdot t} \]
Comparison of time-scales

- history & archaeology
- archaeology & anthropology
- anthropology, evolution, & geology
Chapter 3-2: Carbon Dating Method

Carbon dating is the most frequently used dating technique it measures the present amount of $^{14}\text{C}$ in the sample – $N(t)$ – and compares it with the initial $R=^{14}\text{C}/^{12}\text{C}$ ratio value in the sample – $N_0$. This comparison yields the age of the sample $t$:

$$N(t) = N_0 \cdot e^{-\lambda \cdot t} \quad \Rightarrow \quad \ln \frac{N(t)}{N_0} = -\lambda \cdot t \quad \Rightarrow \quad \ln \left( \frac{N(t)}{N_0} \right)^{-1} = \lambda \cdot t$$

$$t = \frac{1}{\lambda} \cdot \ln \left( \frac{N_0}{N(t)} \right) = \frac{1}{\lambda} \cdot \ln \left( \frac{N\left(^{14}\text{C}\right)_{t=0}}{N\left(^{14}\text{C}\right)_{t=t}} \right) \quad \text{with} \quad N_0 = R \cdot N\left(^{12}\text{C}\right)$$

$$R = \frac{N\left(^{14}\text{C}\right)}{N\left(^{12}\text{C}\right)}$$
Basis of $^{14}$C-Method

- Cosmic Ray bombardment creates free neutrons

- Nuclear reaction with the atmospheric $^{14}$N(n,p)$^{14}$C produces an average ratio of $^{14}$C/$^{12}$C $\approx 10^{-12}$

- Rapid chemical reaction with $O_2$ (21%) in the atmosphere $^{14}$C + 1/2$O_2 \Rightarrow ^{14}$CO + O $^{14}$CO + HO $\Rightarrow ^{14}$CO$_2$ + H

- Average 6-8 years exchange rate with biosphere warrants uniform distribution of $^{14}$C

- Uniform implementation in biomaterial by photosynthesis, breathing, eating etc.
EXAMPLE

START WITH 10 CURIES OF MATERIAL WITH A 30 SECOND HALF LIFE.

HOW MANY CURIES WOULD BE LEFT AFTER 2 MINUTES?
Cosmic Ray Production

The production of $^{14}$C depends on:

- cosmic ray flux (sun activity)
- earth magnetic field (cosmic ray focusing)

Equilibrium between production and decay will be reached which is about 40 tons of $^{14}$C. The total abundance of $^{12}$C has been estimated to about $3.8 \cdot 10^{12}$ tons; the $^{14}$C/$^{12}$C ratio is: $R(^{14}\text{C}/^{12}\text{C}) \approx 10^{-12}$
$^{14}$C distributes through biological and chemical processes in earth material. It binds with Oxygen to form CO$_2$. It mixes rapidly through atmosphere as shown in bomb test and fallout analysis (e.g. Tschernobyl). $^{14}$C mixes with earth surface material in cyclic modes; the cycle time determines the average abundances of $^{14}$C in material. Small fraction of 0.7 tons $^{14}$C is average amount in atmosphere, fast mixing (10 years cycle time) with surface water by evaporation processes and rain warrants similar abundance (1 ton) to be stored in ocean surface water. Deep ocean water is highly enriched (3500 tons) due to slow 10000 years cycle time. Biological exchange through photosynthesis and exchange is about 5 to 10 years, ca 1.1 tons of $^{14}$C is stored in plants and creatures.
Deviation of $^{14}$C from Standard Value

empirical deviations have been observed in comparison with other methods – tree ring method & uranium dating. What is the reason?

10 $\% \Delta^{14}$C translates roughly into 3% age uncertainty
Change in earth magnetic field

The variations in $^{14}$C deviation correlate with the fluctuations in earth magnetic field. The earth magnetic field changes with a $\approx 10000$ y cycle. Field fluctuations cause cosmic ray flux modifications which affect the overall $^{14}$C production rate. The $^{14}$C age deviation can be fit with a sinusoidal curve with a period of $\approx 9000$ y well in agreement with the earth magnetic field period.
Fine structure of deviation

$^{14}$C concentration in Georgian wine during the 40 year period of 1908 to 1952 shows direct correlation with the solar flare activity (number of sunspots shows a 11 year period cycle). Solar flares originate large fraction of cosmic ray flux.
Man-made deviations

Rapid increase of atmospheric $^{14}$C production during nuclear bomb tests.
Modern Times

$^{14}$C content in pre-1950 wines in comparison with atmospheric $^{14}$C. The decline in $^{14}$C is due to the increase of fossil fuel burning by industry and traffic (coal, oil).

$^{14}$C content in vintage whiskies in comparison with atmospheric $^{14}$C from atomic bomb tests.
Rabbits live on grass exposed to the CO$_2$ fumes of car engines burning fossil fuel. The age of the fossil fuel is about 10 Million years with considerable lower $^{14}$C content than average CO$_2$ in air. Photosynthetic absorption into the grass with subsequent feeding and digestion of the local rabbit makes it appear old for the unaware and unobserving $^{14}$C dating analyst.
Methods of $^{14}$C dating

Absolute dating techniques carry too large uncertainties, therefore relative dating by comparison to $^{12}$C content in sample material.

\[
t = \frac{1}{\lambda} \ln \left( \frac{^{14}C(t = 0)}{^{14}C(t)} \right) = 8284 \cdot \ln \left( \frac{^{14}C(t = 0)}{^{14}C(t)} \right)
\]

\[
t = 18500 \cdot \lg \left( \frac{^{14}C/^{12}C(t = 0)}{^{14}C/^{12}C(t)} \right)
\]

$^{14}$C/$^{12}$C abundance at $t=0$ assumed to be $1.3 \cdot 10^{-12}$ but corrected for $^{14}$C variations in time.
A wooden pillar found in a cliff dwelling weights 10 kg, calculate the $^{12}C$ content

1 mole of any kind of material contains $N_A = 6.022 \cdot 10^{23}$ particles (Avogadro’s number)

1 mole of $^{12}C$ has $A = 12 \text{ g}$

The piece of wood has a mass of 10 kg.

This translates into a number of $^{12}C$ atoms:

$$N^{(12\text{C})} = \frac{N_A}{A} \frac{[\text{nuclei/mole}]}{[\text{g/mole}]} \cdot M [\text{g}] =$$

$$= \frac{6.023 \cdot 10^{23}}{12} \frac{[\text{nuclei/mole}]}{[\text{g/mole}]} \cdot 10 \cdot 10^3 [\text{g}]$$

$$N^{(12\text{C})} = 5.02 \cdot 10^{26} \text{ [nuclei]}$$
How can we count the $^{14}$C content?

Three standard methods are applied:
• Liquid Scintillation Spectrometry LSC
• Gas Proportional Counting GPC
• Accelerator Mass Spectrometry AMS

LSC and GPC refer to direct measurements of the $^{14}$C activity, by the use of conventional radiation detection devices (scintillator & proportional counter) to measure the 0.156 MeV low energy $\beta^-$ radiation. AMS is a method to count the number of $^{14}$C atoms from a small sample.
Chemical Preparation for LSC

Sample must be chemically prepared; low energy $\beta$ particles will not be able to leave solid body (internal absorption).

Conversion of sample carbon to counting solvent benzene $C_6H_6$. Mixing with liquid scintillator material. $\beta$ particles are absorbed and converted into light which is detected with photomultiplier systems at a typically 10-40% detection efficiency.
Preparation for GPC

Carbon sample is chemically converted into a CO$_2$ gas and mixed with counting gas of high ionization properties. The activity is detected with a Geiger Counter which measures the electrical signal due to the ionization of the gas from the ionizing effects of the low energy $\beta$ radiation.
Background Problems

Both counting systems, LSC & GPC only count the number of radioactive events. They cannot identify the source of the activity. They only can operate successfully if it is assured that the detected event actually has originated in the $^{14}\text{C}$ decay. That requires background suppression techniques. The main background is originated from the cosmic rays and natural radioactivity contained in the surrounding laboratory environment (walls etc). The detectors therefore must be shielded with lead (or other means) for reducing the background at low count rates.
### Required sample size

<table>
<thead>
<tr>
<th>Material</th>
<th>Conventional (g)</th>
<th>Mini-counting (g)</th>
<th>AMS (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood (whole) (cellulose)</td>
<td>10–25</td>
<td>0.1–0.5</td>
<td>50–100</td>
</tr>
<tr>
<td></td>
<td>50–100</td>
<td>0.5–1.0</td>
<td>200–500</td>
</tr>
<tr>
<td>Charcoal (&amp; other charred materials)</td>
<td>10–20</td>
<td>0.1–0.5</td>
<td>10–100</td>
</tr>
<tr>
<td>Peat</td>
<td>50–100</td>
<td>0.5–1.0</td>
<td>100–200</td>
</tr>
<tr>
<td>Textiles</td>
<td>20–50</td>
<td>0.05–0.10</td>
<td>20–50</td>
</tr>
<tr>
<td>Bone</td>
<td>100–400</td>
<td>2.0–5.0</td>
<td>500–1000</td>
</tr>
<tr>
<td>Shell</td>
<td>50–100</td>
<td>0.5–1.0</td>
<td>50–100</td>
</tr>
<tr>
<td>Sediment, soils</td>
<td>100–500</td>
<td>2.0–10.0</td>
<td>500–25,000</td>
</tr>
</tbody>
</table>

Smaller samples lead to unacceptable uncertainties due to low count rates and large statistical errors!
Statistical Uncertainty

each measured number has a certain statistical uncertainty

\[ \Delta N \approx \sqrt{N} \]
Statistical Limitations

\[ N \pm \sqrt{N} \]

- \( 10000 \pm 100 \) (1%)
- \( 1000 \pm 32 \) (3%)
- \( 100 \pm 10 \) (10%)
- \( 10 \pm 3.2 \) (32%)

As higher the initial sample size, as higher the activity count (for a fixed counting time) as lower the relative counting error \( \sqrt{N} / N \), as lower the statistical uncertainty of the age determination.
Statistical Uncertainty: Example

$$t = \frac{1}{\lambda} \cdot \ln\left( \frac{N_0}{N(t)} \right)$$

- $N_0 = 3200$
- $t_{1/2} = 5730 \text{y}$  \( \lambda = 1.21 \cdot 10^{-4} \text{ y}^{-1} \)
- $N(t) = 100 \pm 10$

$$t = \frac{1}{1.21 \cdot 10^{-4} \text{ y}^{-1}} \ln\left( \frac{3200}{110} \right) = 27855 \text{ y}$$

$$t = \frac{1}{1.21 \cdot 10^{-4} \text{ y}^{-1}} \ln\left( \frac{3200}{90} \right) = 29513 \text{ y}$$

About 1660 years statistical uncertainty at this date; this corresponds to an overall uncertainty of ~6% -7% in age determination!
Due to inherent uncertainties in the $^{14}$C dating method, the results are given in terms of probability distribution, with the half-width of the curve expressing the uncertainty in age determination. The overall probability that the age falls within a specific time window corresponds to the area under the curve. $1\sigma$ means, object has the age of 4000 ± 50 years with 68% probability; $2\sigma$ means age of 4000 ± 100 years with 95% probability; $3\sigma$ etc.