Nuclear Fuel Cycle 2013

Lecture 5: Detection of Ionizing, Radiochemistry

Gas filled detectors

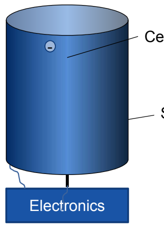
Principle for many of detectors
(GM counters for instance)

Radiation enters chamber

Ionizes gas in chamber

Ions travel towards cathode/anode

=> Currency detected by electronics



Central pin: Anode (or cathode)

Shell: Cathode (or anode)

Electronics

Gas filled detectors

Energy of α–particle is about 4 MeV

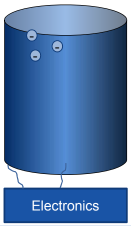
100 000 ionizations

The charge = $10^5 \times 1.602 \times 10^{-19}$ C ~ 10^{-14} A

- The signal needs to be amplified greatly

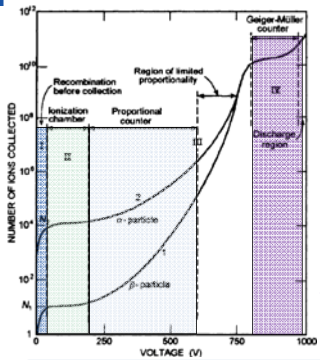
Gas filled detectors

If the potential between anode and cathode is large, the ion will accelerate and initiate secondary ions



=> Stronger signal

Gas filled detectors



I: ions and electrons recombine before reaching electrodes

II: ionization chamber:
1 ionization = 1 signal

III: proportional region:
signal is proportional to primary ionizations

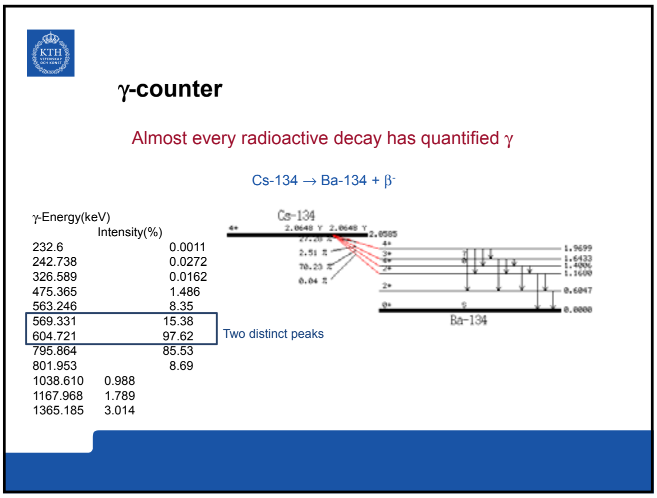
IV: Geiger-Müller counter:
tube is discharged by every ionization

γ-radiation

Gamma radiation has much longer range (lower LET) and will travel through air-filled detector with very few interactions.

Instead: Use denser material in detector:
Semiconductor

- When ionizing radiation interacts with the semiconductor an electron is excited to the conduction band.
  The electron then travels towards the anode.
- Gamma spectrometer (or Multichannel analyzer)



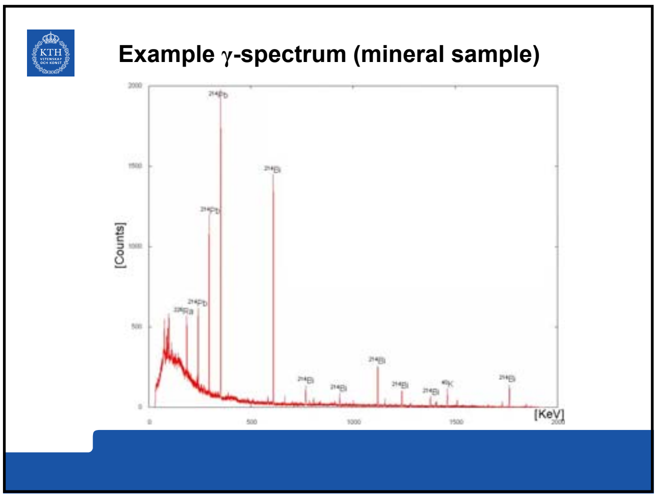
γ-counter

Almost every radioactive decay has quantified γ

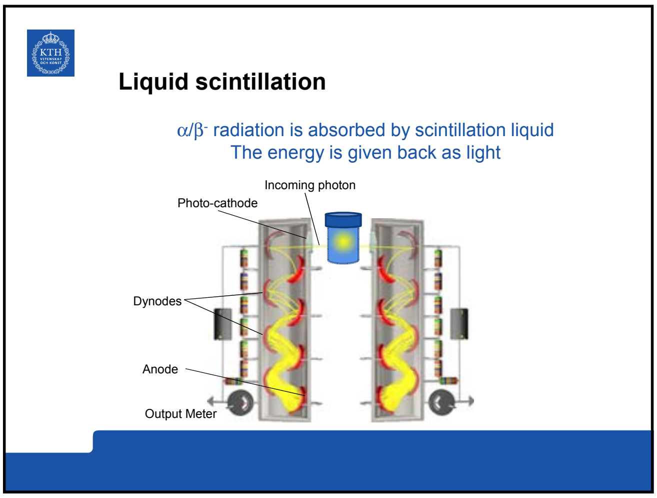
Cs-134 → Ba-134 + β^-

γ-Energy(keV)	Intensity(%)
232.6	0.0011
242.738	0.0272
326.589	0.0162
475.365	1.486
563.246	8.35
569.331	15.38
604.721	97.62
795.864	85.53
801.953	8.69
1038.610	0.988
1167.968	1.789
1365.185	3.014

Two distinct peaks



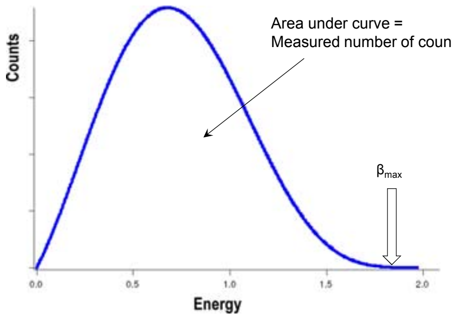
Example γ-spectrum (mineral sample)



Liquid scintillation

α/β^- radiation is absorbed by scintillation liquid
The energy is given back as light

β-spectrum



Area under curve =
Measured number of counts

β_{max}

Efficiency of a detector

Some of the activity will never enter detector due to geometry reasons. This has to be considered but is NOT the efficiency

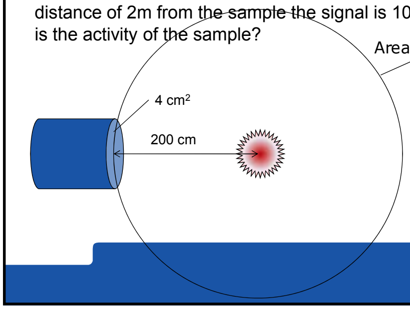
Some radiation will not interact with detector

$$\text{Efficiency} = \frac{\text{What is detected}}{\text{What enters the detector}}$$

NOTE!
Bq is absolute activity.
cps (counts per second) is measured value!

Example

A portable detector is used to measure the activity of a sample. The surface area of the detector is 4 cm^2 and the efficiency is 2 %. At a distance of 2m from the sample the signal is 10 counts per second. What is the activity of the sample?



$$\text{Area of sphere} = 4\pi R^2 = 502654\text{cm}^2$$

Fraction that enters detector=
$4/502654 = 8\times10^{-6}$

$$A = \frac{10}{0.02\times8\times10^{-6}} = 62.8\text{MBq}$$

Radiochemistry I

The use of radioactive isotopes (radionuclides) as tracers to follow chemical processes

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Why are radionuclides used?

- The exact same element is used, it has the same chemical and physical properties
- Radionuclides are independent of pressure, temperature, chemical and physical state
- Radionuclides are easy to detect and are measured with high precision

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With radionuclides low amounts can be detected

$$A = N\lambda \quad \Longleftrightarrow \quad m = A\frac{M}{\ln 2 \, N_A} t_{½}$$

Assume that 1 Bq can be measured with sufficient accuracy:

$t_{½}$	Number of atoms	mol
1 h	5 200	8.64×10^{-21}
1 d	125 000	2.08×10^{-19}
1 y	4.55×10^{7}	7.55×10^{-17}
10^{5} y	4.55×10^{12}	7.55×10^{-12}
10^{9} y	4.55×10^{16}	7.55×10^{-8}

Why are radionuclides used?

- The exact same element is used, it has the same chemical and physical properties
- Radionuclides are independent of pressure, temperature, chemical and physical state
- Radionuclides are easy to detect and are measured with high precision
- Does not affect the system (if activity is not too high)
- No interference of other elements
- Cheap (compared with for instance ICP-MS)

Issues to keep in mind when working with very low concentrations

- Adsorption to walls of vessel
- Formation of radiocolloids
- Equilibrium reactions
  $m\mathrm{UO_2}^{2+} + p\ \mathrm{H_2O} \leftrightarrows \mathrm{(UO_2)_m(OH)_p}^{2m-p} + p\ \mathrm{H^+}$s
  at mM U-conc. 50% is $\mathrm{(UO_2)_m(OH)_p}^{2m-p}$
  at μM U-conc. $\mathrm{(UO_2)_m(OH)_p}^{2m-p}$ is negligible
- Precipitation
  $\mathrm{La(OH)_3}(s) \leftrightarrows \mathrm{La^{3+}} + 3\ \mathrm{OH^-}$ $K_{s0}=10^{-19}\ \mathrm{M}^4$

  At $[\mathrm{OH^-}]$= 1 mM does 100 MBq/l $^{130}\mathrm{La}^{3+}$ not exceed solubility product

Working with radionuclides ALARA

As
Low
As
Reasonable
Achievable

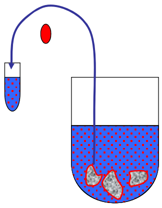
Working with radionuclides
Carrier

A non-radioactive carrier is usually added to a system to ensure normal chemical behavior

Isotopic exchange
$AX + BX^* \Leftrightarrow AX^* + BX$
is required

Example

Determination of Sr-distribution between granite and solution



Water

Add granite

Add tracer (Sr-90)

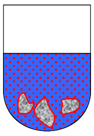
Wait for equilibrium

Take sample from solution

Sr-90 is a β^--emitter with
β_{max} at 550 keV
$t_{1/2}$ = 28.5 y

Example continued

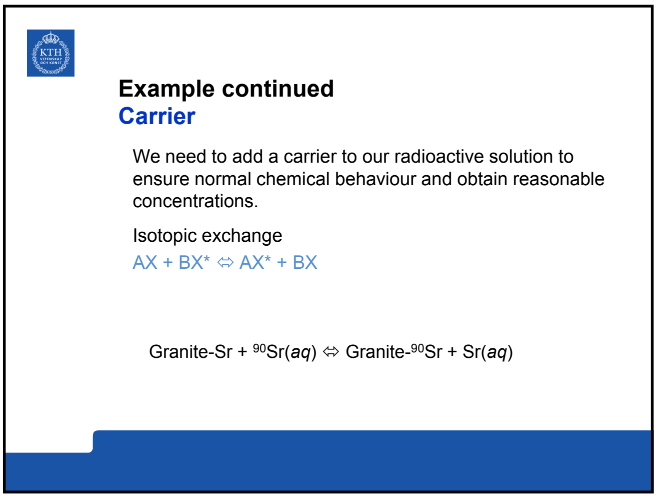
Determination of distribution of cation between granite and solution



To be able to detect the radionuclide,
a reasonable concentration of radionuclide would be very low (nM or lower, depending on $t_{1/2}$)

⇒ Very low concentrations: any sorption to glass wall or other loss of radionuclide would have large impact

Adding 10^6 times more radionuclide to obtain a reasonable concentration would cause significant water radiolysis which would change the system



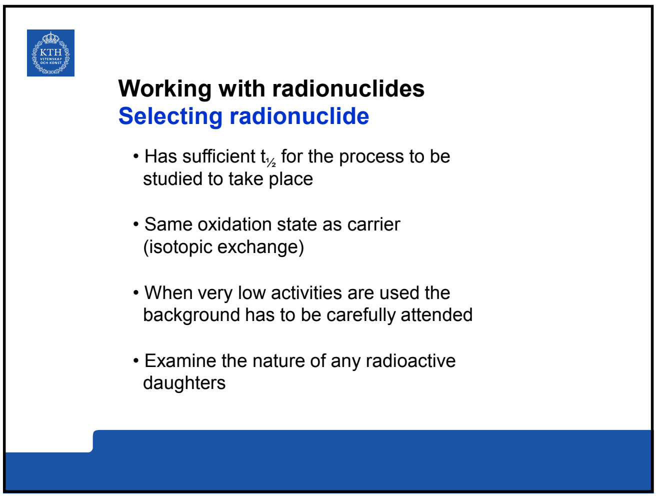
Example continued
Carrier

We need to add a carrier to our radioactive solution to ensure normal chemical behaviour and obtain reasonable concentrations.

Isotopic exchange

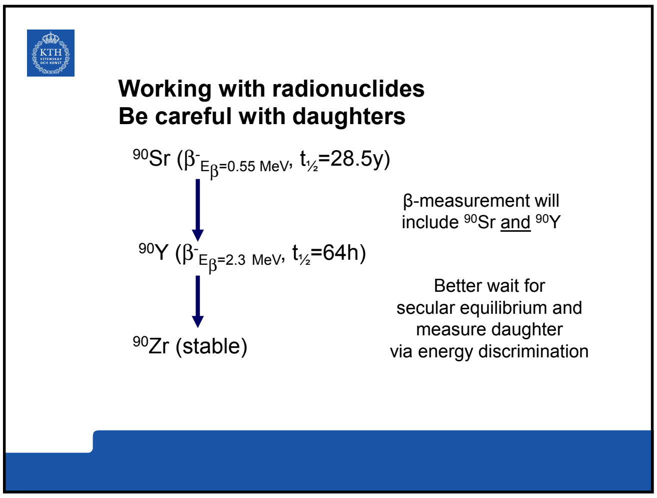
$AX + BX^* \Leftrightarrow AX^* + BX$

Granite-Sr + ^{90}Sr(*aq*) ⇔ Granite-^{90}Sr + Sr(*aq*)



Working with radionuclides
Selecting radionuclide

- Has sufficient $t_{1/2}$ for the process to be studied to take place
- Same oxidation state as carrier (isotopic exchange)
- When very low activities are used the background has to be carefully attended
- Examine the nature of any radioactive daughters



Working with radionuclides
Be careful with daughters

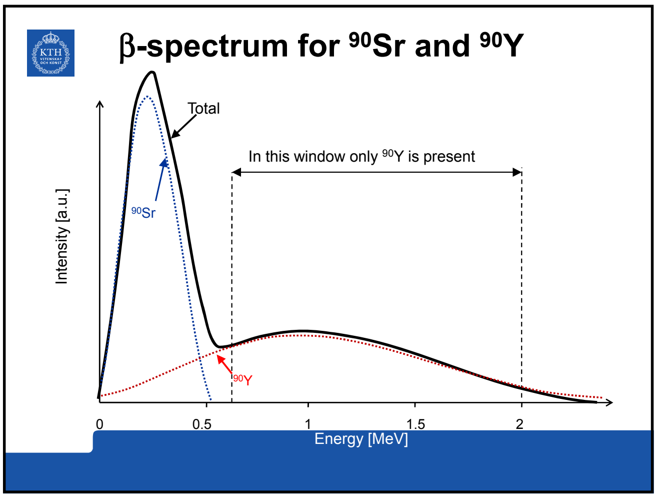
^{90}Sr ($\beta^-_{E_\beta=0.55\text{ MeV}}$, $t_{1/2}$=28.5y)

^{90}Y ($\beta^-_{E_\beta=2.3\text{ MeV}}$, $t_{1/2}$=64h)

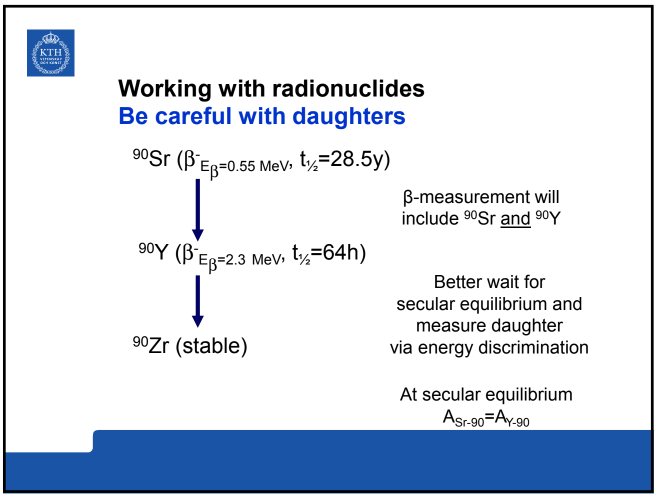
^{90}Zr (stable)

β-measurement will include ^{90}Sr and ^{90}Y

Better wait for secular equilibrium and measure daughter via energy discrimination



β-spectrum for ^{90}Sr and ^{90}Y



Working with radionuclides
Be careful with daughters

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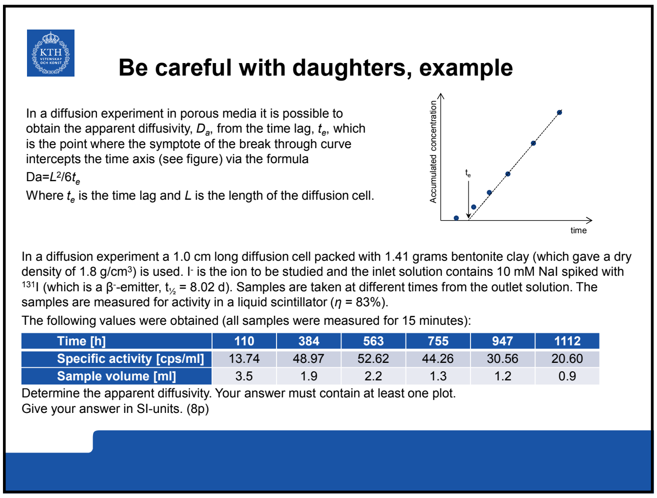
^{90}Zr (stable)

β-measurement will
include ^{90}Sr and ^{90}Y

Better wait for
secular equilibrium and
measure daughter
via energy discrimination

At secular equilibrium
$A_{Sr\text{-}90}=A_{Y\text{-}90}$



Be careful with daughters, example

In a diffusion experiment in porous media it is possible to obtain the apparent diffusivity, D_a, from the time lag, t_e, which is the point where the symptote of the break through curve intercepts the time axis (see figure) via the formula

$D_a=L^2/6t_e$

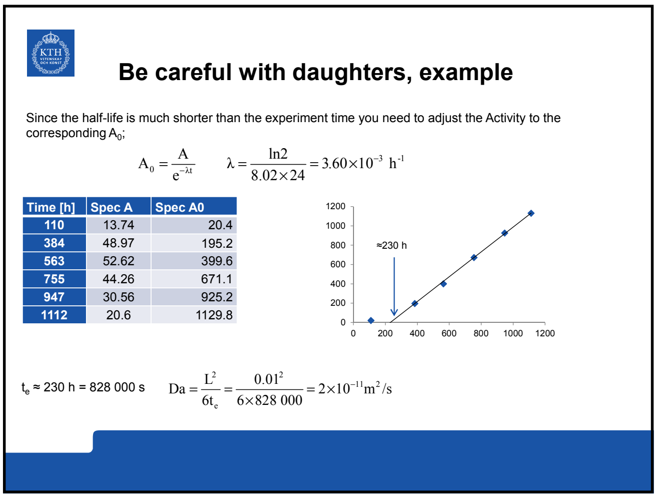
Where t_e is the time lag and L is the length of the diffusion cell.

In a diffusion experiment a 1.0 cm long diffusion cell packed with 1.41 grams bentonite clay (which gave a dry density of 1.8 g/cm^3) is used. I$^-$ is the ion to be studied and the inlet solution contains 10 mM NaI spiked with ^{131}I (which is a β$^-$-emitter, $t_{½}$ = 8.02 d). Samples are taken at different times from the outlet solution. The samples are measured for activity in a liquid scintillator (η = 83%).

The following values were obtained (all samples were measured for 15 minutes):

Time [h]	110	384	563	755	947	1112
Specific activity [cps/ml]	13.74	48.97	52.62	44.26	30.56	20.60
Sample volume [ml]	3.5	1.9	2.2	1.3	1.2	0.9

Determine the apparent diffusivity. Your answer must contain at least one plot.
Give your answer in SI-units. (8p)



Be careful with daughters, example

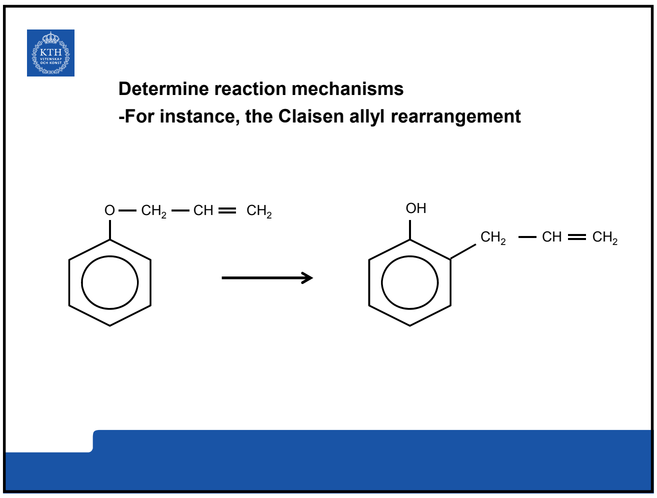
Since the half-life is much shorter than the experiment time you need to adjust the Activity to the corresponding A_0;

$$A_0 = \frac{A}{e^{-\lambda t}} \qquad \lambda = \frac{\ln 2}{8.02 \times 24} = 3.60 \times 10^{-3}\ \mathrm{h}^{-1}$$

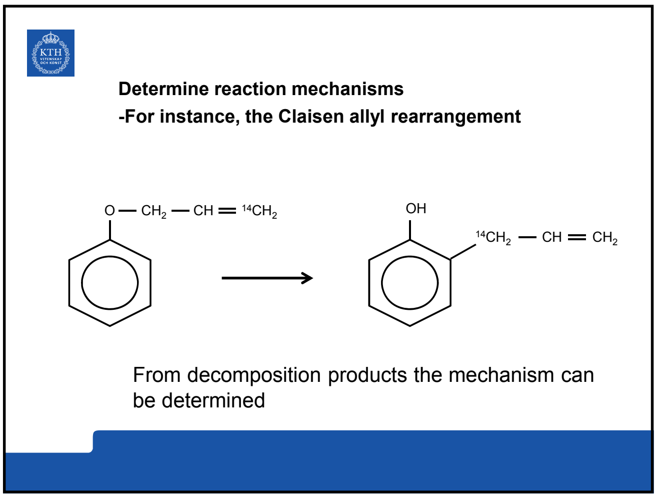
Time [h]	Spec A	Spec A0
110	13.74	20.4
384	48.97	195.2
563	52.62	399.6
755	44.26	671.1
947	30.56	925.2
1112	20.6	1129.8

$t_e \approx 230$ h = 828 000 s

$$Da = \frac{L^2}{6t_e} = \frac{0.01^2}{6 \times 828\,000} = 2 \times 10^{-11} \mathrm{m}^2/\mathrm{s}$$

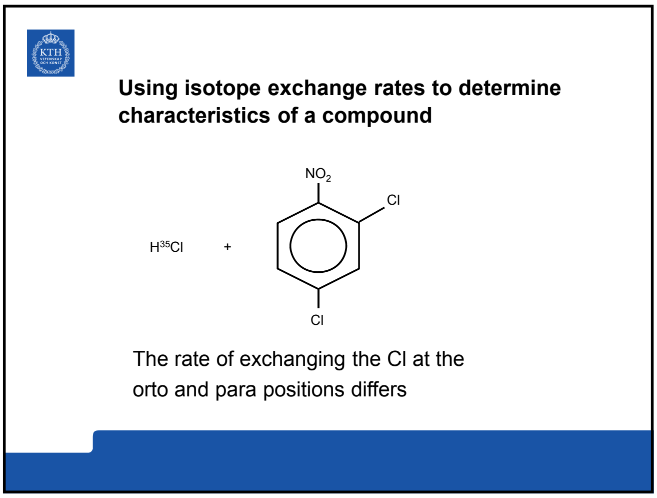


Determine reaction mechanisms
-For instance, the Claisen allyl rearrangement



Determine reaction mechanisms
-For instance, the Claisen allyl rearrangement

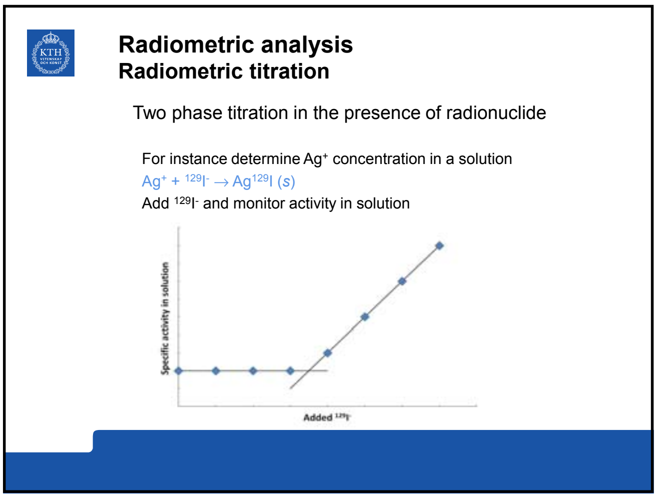
From decomposition products the mechanism can be determined



Using isotope exchange rates to determine characteristics of a compound

$H^{35}Cl$ +

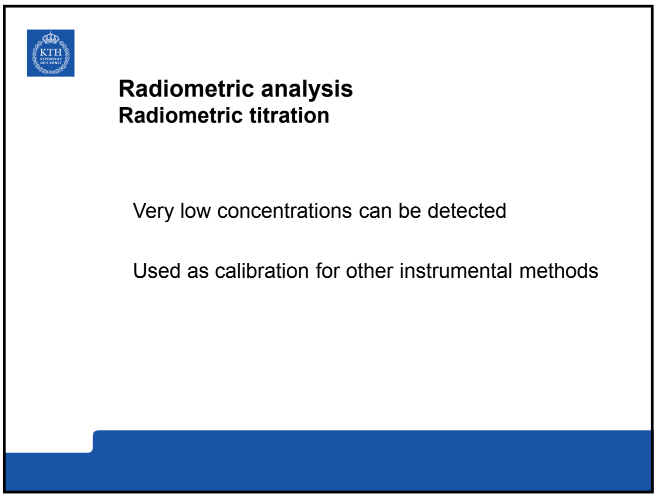
The rate of exchanging the Cl at the orto and para positions differs



Radiometric analysis
Radiometric titration

Two phase titration in the presence of radionuclide

For instance determine Ag^+ concentration in a solution
$Ag^+ + {}^{129}I^- \rightarrow Ag^{129}I\ (s)$
Add ${}^{129}I^-$ and monitor activity in solution



Radiometric analysis
Radiometric titration

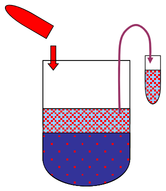
Very low concentrations can be detected

Used as calibration for other instrumental methods

Isotope dilution

Used when quantitative separation of one compound is not possible

Qualitative separation is needed, though



System with element of unknown mass w_u

Add known weight (w_0) RN (same element)

Selectively separate element for instance via extraction

Take sample and measure activity and mass (Specific activity, S_m)

Isotope dilution

The specific activity is the same in the whole system.

$$S_m = S_{system} = \frac{\text{Total activity}}{\text{Total weight}} = \frac{w_0 S_0}{w_u + w_0}$$

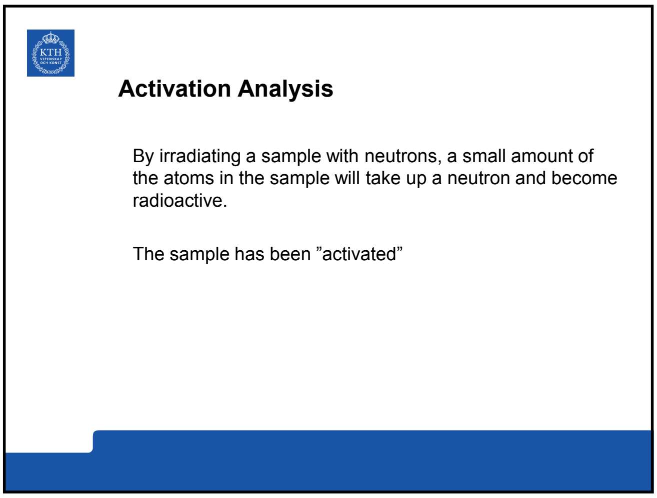
And the unknown weight can be calculated from

$$w_u = \left(\frac{S_0}{S_m} - 1\right) w_0$$

Isotope dilution
Applications

Determine

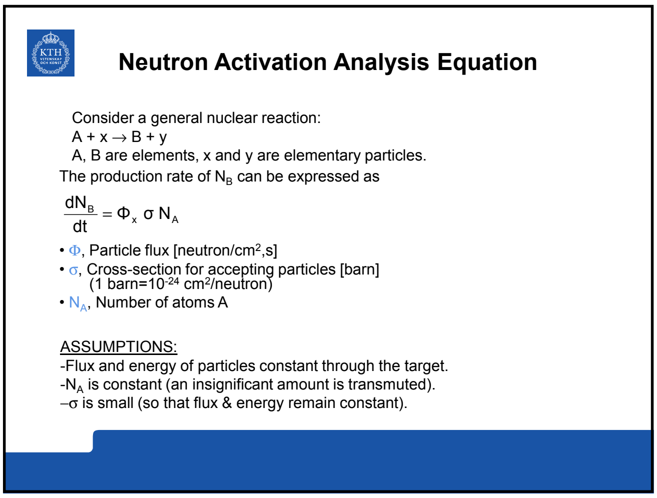
- The naphtalene concentration in tar
- Fatty acids in mixtures of natural fat
- Amino acids in biological material



Activation Analysis

By irradiating a sample with neutrons, a small amount of the atoms in the sample will take up a neutron and become radioactive.

The sample has been ”activated”



Neutron Activation Analysis Equation

Consider a general nuclear reaction:
$A + x \rightarrow B + y$
A, B are elements, x and y are elementary particles.

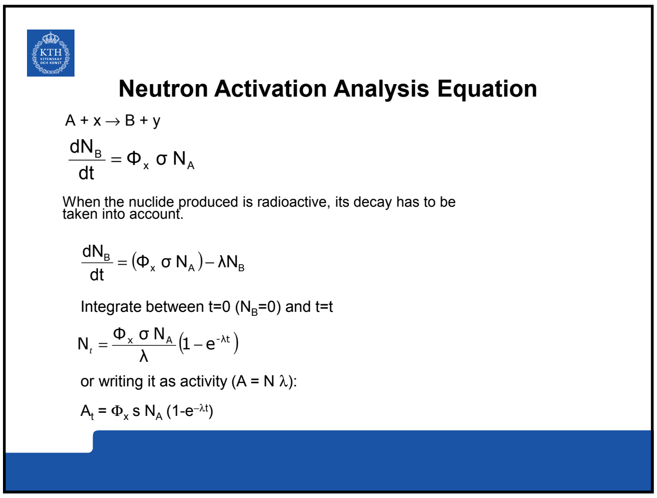
The production rate of N_B can be expressed as

$$\frac{dN_B}{dt} = \Phi_x \sigma N_A$$

- Φ, Particle flux [neutron/cm^2,s]
- σ, Cross-section for accepting particles [barn]
  (1 barn=10^{-24} cm^2/neutron)
- N_A, Number of atoms A

<u>ASSUMPTIONS:</u>

-Flux and energy of particles constant through the target.
-N_A is constant (an insignificant amount is transmuted).
–σ is small (so that flux & energy remain constant).



Neutron Activation Analysis Equation

$A + x \rightarrow B + y$

$$\frac{dN_B}{dt} = \Phi_x \sigma N_A$$

When the nuclide produced is radioactive, its decay has to be taken into account.

$$\frac{dN_B}{dt} = \left(\Phi_x \sigma N_A\right) - \lambda N_B$$

Integrate between t=0 (N_B=0) and t=t

$$N_t = \frac{\Phi_x \sigma N_A}{\lambda}\left(1 - e^{-\lambda t}\right)$$

or writing it as activity ($A = N \lambda$):

$A_t = \Phi_x s N_A (1-e^{-\lambda t})$

Neutron Activation Analysis Equation

$$A_t = \Phi_x \, \sigma \, N_A \left(1 - e^{-\lambda\lambda}\right)$$

The produced radionuclide will decay and we have to acccount for the activity loss:

$A_{t,t'}=A_t \, e^{-\lambda t'}$

We get

$A = \Phi \, \sigma \, N_A \, (1-e^{-\lambda t_{irr}}) \, e^{-\lambda t_{cool}}$

NAA Example

5 g. Chrome is irradiated for 3 hours in a neutron flux of 10^{13} n/cm^2,s.
What is the activity 48 hours after the irradiation?

$A = \Phi \, \sigma \, N_A \, (1-e^{-\lambda t_{irr}}) \, e^{-\lambda t_{cool}}$

Φ = 10^{13} n/cm^2,s

σ = ?
N = ? (total amount Cr=5/52*6*10^{22})
What is the amount of each isotope of Cr?

Segré or
http://atom.kaeri.re.kr/ton/

NAA Example

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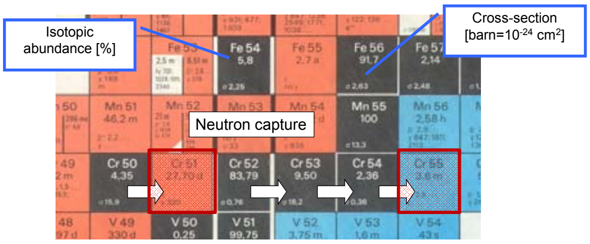

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Stable Isotopes	Cr-50	Cr-52	Cr-53	Cr-54
Isotopic abundance [%]	4.35	83.79	9.5	2.36
$t_{1/2}$ of neutron activated product	27.7 d	stable	stable	3.5 min
Cross section [barn]	15.9	0.76	18.2	0.36

Only Cr-51 will be radioactive after 48 hours

NAA Example

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What is the activity 48 hours after the irradiation?

$A = \Phi \, \sigma \, N_A \, (1-e^{-\lambda t_{irr}}) \, e^{-\lambda t_{cool}}$

$$\left.\begin{array}{l} \Phi = 10^{13}\ \text{n/cm}^2\text{,s} \\ \sigma = 15.9 * 10^{-24}\ \text{cm}^2\text{/n} \\ N = 5 / 52 * 6*10^{23} * 0.0435 = 2.5*10^{21} \\ \lambda = \ln 2 / (27.7*24*3600) = 2.9*10^{-7}\ \text{s}^{-1} \\ t_{irr} = 3*3600 = 10\ 800\ \text{s} \\ t_{cool} = 48*3600 = 172\ 800\ \text{s} \end{array}\right\} \quad A = 1.19\times10^{9}\ \text{Bq}$$

A = 1.2 GBq

Advantages with NAA

- Highly sensitive
- Nondestructive
- Determination of elements in complex samples;

- Environmental samples
- Mineral samples
- Archeological samples

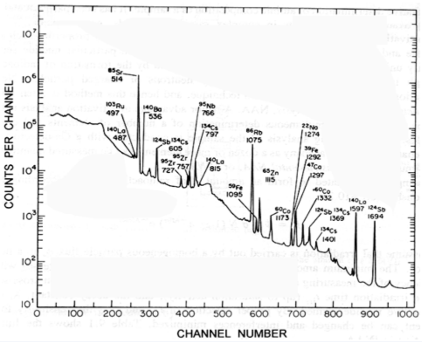
Example

Environmental history of waters in Sweden

1. Mussels were collected from rivers and lakes in Sweden.
   Mussels build shell thicker each year;
   The composition of the shell reflects the water chemistry.
2. Shells were sliced.
3. Sent to neutron irradiation source.
4. Sample was measured directly at arrival from reactor
   (short lived nuclides dominate spectrum).
5. Sample was measured 2 weeks after irradiation
   (short lived nuclides not present anymore).
6. Evaluation of the spectra.

Example

Environmental history of waters in Sweden



Workshop

Calculate tasks 3, 5, 8, 11, 13, 16

And be prepared to calculate on the whiteboard in front of the class.